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COMBUSTION TRIALS WITH SYNCRUDE COKE AND MINTO COAL IN THE MINERAL SCIENCES LABORATORIES CIRCULATING FLUIDIZED BED COMBUSTOR: SULPHUR AND METALS CAPTURE AND METALLIC CORROSION

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COMBUSTION TRIALS WITH SYNCRUDE COKE AND MINTO COAL IN THE MINERAL SCIENCES LABORATORY CIRCULATING FLUIDIZED BED COMBUSTOR: SULPHUR AND METALS CAPTURE AND METALLIC CORROSION

by

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ABSTRACT

Syncrude byproduct coke and Minto coal were combusted with limestone addition in a 100 mm diameter, 2800 mm high pilot-scale circulating fluidized bed combustor. The objective was to investigate the emissions of SO2 and heavy metals, their capture with limestone sorbents and metallic corrosion. With Fort McMurray limestone in a Ca/S = 2.0, greater than 90% of the SO2 was captured and 93% of the vanadium and all of the nickel were accounted for in the ashes. The sulphur capture with Elmtree and Havelock limestones was in the 70-75% range with a Ca/S = 2.0.

Sulphidation-oxidation type corrosion occurred with 304 stainless steel probes exposed for 125 h at the combustor temperature of 850°C. The type and degree of corrosion was similar for both fuel trials, and also similar to that found in tests in bubbling fluidized bed units. There was no evidence of accelerated corrosion attributable to the vanadium content of the coke.

Keywords: Circulating fluidized bed combustion, byproduct petroleum coke, limestone, SO_2 capture, vanadium, corrosion

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ESSAIS DE COMBUSTION AVEC DU COKE DE SYNCRUDE ET DU CHARBON DE MINTO DANS LA CHAMBRE DE COMBUSTION À LIT FLUIDISÉ CIRCULANT DES LABORATOIRES DES SCIENCES MINÉRALES : CAPTURE DU SOUFRE ET DES MÉTAUX ET CORROSION DES MÉTAUX

par

C.A. Hamer*, D.T. Liang** et J.B. Kearns***

RÉSUMÉ

Le coke de sous-produit de Syncrude et le charbon de Minto ont subi des essais de combustion avec un additif de calcaire dans une installation pilote de combustion à lit fluidisé circulant, mesurant 2 800 mm de hauteur et ayant un diamètre de 100 mm. Le but de ces essais était d'examiner les émissions de SO_2 et de métaux lourds, leur taux de capture avec des sorbants du calcaire et la corrosion des métaux. Pour ce qui est du calcaire de Fort McMurray ayant un rapport Ca/S égal à 2,0, au-delà de 90 % du SO_2 était capturé, et 93 % du vanadium et tout le nickel étaient trouvés dans les cendres. La capture du soufre avec des calcaires de Elmtree et de Havelock se situait entre 70 % et 75 % avec un rapport Ca/S égal à 2,0.

La corrosion par sulfuration et par oxydation s'est produite sur 304 sondes en acier inoxydable exposées pendant 125 h à une température de 850°C dans la chambre de combustion. Le type et le degré de corrosion étaient semblables pour les deux essais sur les combustibles et étaient également similaires à ceux obtenus lors des essais effectués dans les systèmes de combustion à lit fluidisé bouillonnant. Aucune preuve ne laissait croire que la corrosion accélérée était attribuable au vanadium contenu dans le coke.

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INTRODUCTION

Byproduct coke from tar sands extraction operations and residuals from heavy oil upgrading plants contain high concentrations of sulphur and heavy metals, particularly vanadium. These impurities can cause problems in the combustion of these materials due to high sulphur dioxide emissions and possible accelerated corrosion associated with vanadium compounds. However, the high califoric value of these byproducts make them attractive as fuels provided they can be burned efficiently in a system which will contain sulphur and heavy metals as innocuous compounds.

CANMET has investigated circulating fluidized bed combustion (CFBC) as a technology to utilize byproduct coke from Syncrude Canada Ltd. F. Friedrich et al (1) and D. Desai et al (2) have described CANMET's work on this fuel and the two contracts (one in 1981 and the other in 1986) with the Hans Ahlstrom Laboratory in Finland for pilot-scale trials in a circulating fluidized bed. The results were very encouraging, giving high combustion efficiency and greater than 90% sulphur capture with a Ca/S mole ratio less than 2. However, these trials did not supply information on vanadium corrosion nor an accurate material balance of the heavy metals. Combustion trials of this coke at Queen's University in a pilot-scale bubbling fluidized bed showed that the bubbling bed technology was not as efficient as the circulating bed for this fuel (3).

In this study, a 100 mm diameter by 2.8 m high pilot-scale circulating fluidized bed combustor has been designed, constructed and operated in the Mineral Sciences Laboratory (MSL). The purpose of this project was to investigate emissions of SO_2 and heavy metals, eg V, Ni, their capture with sorbents and corrosive effects. The first project for this CFBC was an investigation of the combustion of Syncrude byproduct petroleum coke.

Syncrude coke contains 6 to 8% sulphur as well as vanadium and nickel such that upon combustion the resulting ash is about 3% V_2O_5 and 1.5% NiO. There was some concern that this relatively large quantity of vanadium, when combined with sodium, sulphur and oxygen, had the potential of causing catastrophic metallic corrosion in combustors. These elements are capable of forming low melting temperature compounds, as low as 538°C, which can dissolve the protective metal oxide layer and act as an oxygen carrier to replenish the oxygen at the metal surface of boiler tubes (4). Such vanadic corrosion is well documented for boilers which burn residual fuel oils (5,6).

A different type of corrosion mechanism appears to operate in fluidized bed combustors. It has been termed "sulphidation-oxidation" and is associated with low oxygen, high sulphur gaseous environments which may be present at times within the bed (7). High sulphur, low oxygen conditions may also be present at the metal interface under an impervious deposit of sulphated lime and ash. Under these circumstances the protective oxide layer on some alloys, eg nickel and cobalt, can be reduced to sulphides thus corroding the metal.

All the published information on corrosion in fluidized beds is based on work done in bubbling beds. No documented work has been found in the literature on corrosion in circulating fluidized bed systems. Additionally, little data exist on the behaviour of vanadium compounds during fluidized bed combustion of high vanadium fuels. The attempts at material balances for vanadium in the two Ahlstrom tests were not very successful. Better results were obtained in combustion trials of Syncrude coke conducted in Queens University's 0.155 sq m AFBC. In three tests an average of 92.3% of the vanadium and 92.0% of the nickel were accounted for in the bed ash, cyclone drain and the baghouse dust (3). Plass et al reported on successful combustion trials on fluid coke in a pilot CFB but gave little detail (8). In a recent paper, Johnson (9) discusses the combustion of asphaltene containing 1347 ppm vanadium in a circulation boiler. He quotes vanadium capture of 97% from heavy fuel oil residue combusted in a fluidized bed with limestone. The vanadium is captured as calcium vanadate, a high melting point compound. After another test with petroleum coke, this pilot plant was completely dismantled. There was no evidence of vanadium deposition on the tubes or the alumina bed material. No work has been found on vanadium induced corrosion in either bubbling or circulating FBC.

A series of tests were run with Syncrude coke in the small MSL circulating bed unit to determine whether this fuel would cause vanadic corrosion. The size and design of the system permits accurate material balances of both solids and gases. Corrosion probes were installed to determine the nature of short

term corrosion and of the deposits. A second series of combustion tests were made with Minto coal, which contains negligible amounts of vanadium, and a variety of New Brunswick limestones. This series was used as the control for the corrosion probes. The Minto trials were also conducted to determine the optimum limestone, size and source, for use in the new 22 MeW CFBC unit at Chatham, N.B.

This paper will describe MSL's circulating fluidized bed combustor and the results of combustion trials with both fuels. An evaluation of the corrosion probes by the Corrosion Section of the Physical Metallurgy Research Laboratory (PMRL) is also included.

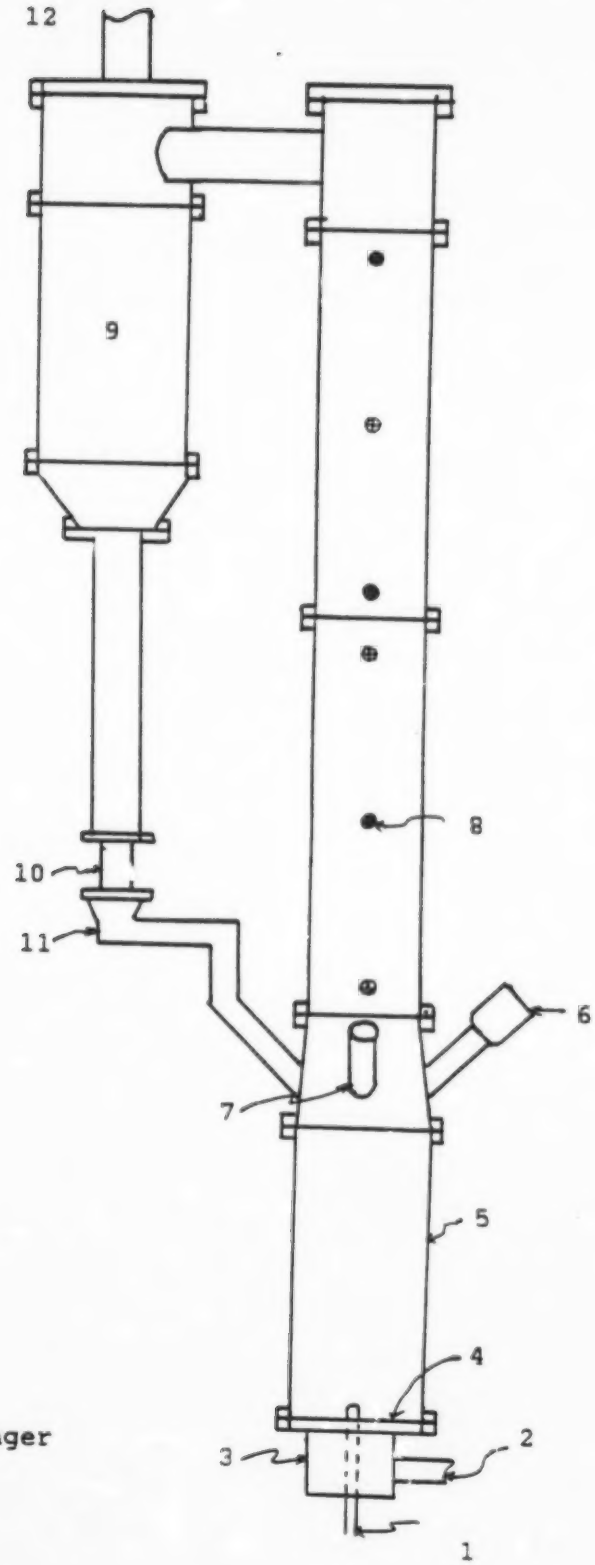
APPARATUS

CIRCULATING FLUIDIZED BED COMBUSTOR

The circulating fluidized bed, as shown schematically in Figure 1, consists of a combustion column, a high temperature cyclone with a hot solids return leg, a heat exchanger and a baghouse. A brief description of the major components follows.

Combustor Column

The combustor column is composed of three sections: a 152 mm diameter by 610 mm high expanded or dense bed section at the bottom; a transition section, 300 mm high, which reduces the diameter to 100 mm; and a 1830 mm high section of 100 mm diameter tube. The total height is presently 2800 mm although there is the capability to increase this to 4620 mm. The expanded bed



1 - pneumatic feed
2 - fluidizing air
3 - windbox
4 - distributor
5 - electric heater
6 - propane burner
7 - sight port
8 - corrosion probes
9 - cyclone
10 - sight glass
11 - air ejector
12 - exhaust to heat exchanger and baghouse

Fig. 1 - MSL's pilot-scale CFBC

section is of stainless steel; all the other sections are ceramic tubes cast with insulating refractory inside 250 mm diameter steel pipes. The sections are flanged and bolted together. The entire combustor is suspended from the ceiling of the laboratory to allow it to expand upon heating.

Air is supplied by a Roots Blower to the combustor through a distributor with thirty-three nozzles. The distributor is machined to a conical concave bottom with a drain pipe for ash in the center. Secondary air is added at the transition section. This expanded bottom section provides a more stable operation in the CFBC. The twofold cross-sectional area and the diverted portion of air to the secondary inlet makes it possible to operate the dense bed at 1/2 to 1/4 of the fluidizing velocity of the upper combustion column. This prevents the bed from being blown away at high fluidizing velocities, a phenomena known to occur when pneumatic transport is in effect which causes the bed to empty in a short time. It also reduces the tendancy for slugging to occur, a consideration especially important for small scale units such as the present one.

Recycle System

The solids-laiden combustion gases pass through a ceramic lined, high temperature cyclone. The internal diameter is 175 mm at the top 260 mm section and reduces to 135 mm diameter over a 760 mm bottom length. A length of 35 mm diameter quartz tube in the down pipe from the bottom of the cyclone allows visual observation of the hot recycle solids. The recycle line runs horizontally for 250 mm and then enters the transistion zone of the

combustor at a 45 angle. Solids movement is controlled by an air injector in the horizontal section of the recycle line.

After the Syncrude coke tests, the recycle system was improved by incorporating a Ramsey Rec level monitor near the bottom cone of the cyclone. This monitor operates with a radioactive source located on one side of the cyclone and a gamma ray detector on the opposite side. A high solids level energizes a solenoid which increases the injector air flow thus increasing the recycle solids rate.

Material Feed System

There are several options for material feeding to the combustor. Coarse material may be fed overbed through the transition section with a screw conveyor, whereas fine material is fed pneumatically either overbed or up through the center of the distributor. Pneumatic feeding under bed is difficult because the feed rate is affected by the pressure drop within the bed and consequently this method was abandoned. Very fine material tends to pack in a hopper and screw conveyor feed system. To overcome this problem a small fluidized bed is used to hold very fine material in suspension while an injector within this bed fed material to the combustor. The operation of the injector is controlled by a timer and solenoid, which in turn, allow control of the feed rate. This fluidized bed feeder is itself fed by a screw conveyor to maintain a more or less constant bed level. The entire feeding system sits on a weigh scale. This system was used to feed the Syncrude coke - limestone blend.

Because the Minto coal was coarser than the coke, it was not necessary to use the fluidized bed feeder. Instead a screw feeder feeds material via an injector system to the recycle line just before it enters the combustor.

A screw conveyor at the bottom of the recycle line below the cyclone permits regulated removal of ash from the unit. Coarse ash may be drained through the distributor.

Heat Exchanger

A vertical tube and shell heat exchanger is used to cool the exhaust gas to within the limit of the operation of the baghouse. The gas passes through the inside of the 25 mm steel tubes, and the water circulates in the outer shell. Four drain taps allow the use of the fraction of the 2.5 sq m heat exchange surface area required to cool the gas.

The heat exchanger also acts as a gravity settling chamber because it cools the gas thus reducing its velocity. These solids are removed through a drain tap at the bottom of the exhanger.

Baghouse

The cooled exhaust gases pass through an American Air FIlter baghouse with nine bags having a total filter area of 4.7 sq m and a maximum operating temperature of 200^{o}C.

Gas Analysis

The CFB test unit is equipped with the following gas analyzers: Oxygen analyzer, Beckman, model # 755

CO/CO_2 analyzer, Infared Industries, model IR-702

SO_2 analyzer, Western Research, model 721A

The gas sample is drawn through a Pall filter cartridge downstream of the hot cyclone by a vacuum pump. A refrigeration unit and a Purma-pure dryer are installed in the line to remove moisture. Outputs from the analyzers, along with the thermocouple readings, are collected by a Taurus data processor and stored in a microcomputer. The instaneous readings are displayed on the computer screen and the two-minute running averages are printed out and also stored on diskettes.

The analysers are calibrated daily by diluting pure SO_2, CO, CO_2 and O_2 with N_2 to the appropriate concentrations through mass flow controllers. The SO_2 analyser is rechecked half-way through a run.

Start-up Heaters

An 8 kW electric heater coil wound around the stainless steel pipe provides most of the heat required to bring the bed temperature to about 700°C at which point coal is added. A propane burner, whose flame is stabilized with a small flow of hydrogen to prevent blowout, is located in the transition section and assists in initial heating.

Corrosion Probes

The middle three of the five pressure taps in the combustion

column are also used as corrosion probes. These three probes are 12.8 mm diameter by 0.95 mm wall thickness, ASTM A213/269 type 304 HT stainless steel seamless pipe. The nominal composition is: 8.0-11.0% Ni, 18.0-20.0% Cr, 0.08% max C, 2.00% max Mn, 0.040% max P, 0.030% max S and 0.75% max Si. All the probes were cut from the same length of tube. The probes extend across the diameter of the 100 mm combustor section. The open end of the tubes have a quartz wool plug to keep dust out of the manometers. At the end of the tests with the Syncrude coke the probes were removed and new ones inserted for the Minto coal control trials.

EXPERIMENTAL PROCEDURE

PROCEDURE FOR SYNCRUDE COKE COMBUSTION TESTS

The pilot-scale circulating fluidized bed was operated on a one shift basis. The electric heater surrounding the bottom section was maintained at 600°C overnight, but with no fluidizing air through the system, the remainder of the unit was cool. A bed of 7000 g sulphated limestone was retained from a previous run. At startup the heater temperature was increased to 900°C, the propane burner was ignited and a minimum of fluidizing air was admitted to the combustor. After approximately an hour the bed temperature was 700°C and the overbed feeding of a sub-bituminus coal was started at a low rate. As the temperature in the bed and in the combustor column increased, the coal feed rate and the fluidizing air were also increased. Because the petroleum coke is so unreactive, it was necessary for the combustor temperature to be above 800°C in order for the coke to burn satisfac-

torily. The coke feed rate was increased and the coal feed rate was decreased until at 850 -870°C only coke was being fed. The propane burner was turned off and power to the electric heater decreased. The total time for this startup procedure was normally 2 - 2 1/2 h.

A smooth, steady state operation was achieved with a feed rate of 5 - 5.5 kg/h blended coke-limestone (Ca/S ratio = 2.0) and a fluidizing velocity of 3 - 3.5 m/s in the 100 mm diameter combustor column. The temperature in the combustor was readily maintained at 850 - 880°C with a relatively small 10 - 15°C temperature differential between the bottom and top of the combustor, the latter being the hotter. Some cooling occurred though the cyclone and recycle line such that the temperature of the solids decreased by a 100°C or more before re-entering the combustion column.

Because the exhaust gas passing through the vertical heat exchanger is cooled, thus reducing its velocity, and changes direction by 90 degrees at the bottom of the heat exchanger, solids disengage from the gas and fall to the bottom. These are drained at regular intervals. The remainder of the dust particles collect in the baghouse. The container for the baghouse dust was usually changed halfway through the run.

At the conclusion of each test run, the ash was drained from the bed, heat exchanger and baghouse, weighed and sampled for analysis. Seven kilograms of the bed ash was returned to the combustor for the startup of the next test.

As the initial combustion trials were used to prove-in and modify the system few samples were taken for ash analysis. The final 15 runs were sampled to obtain material balances on Ca, S, Ni, and V. Sulphur capture was also calculated from the gas analysis. The Ca/S ratio was maintained at 2.0 for all tests and the superficial velocity was between 3.1 and 3.6 m/s.

Procedure for Minto Coal Combustion Tests

Principally due to the larger size of the coal compared to the coke and also the greater reactivity of the coal, some minor changes to the system and operating procedure were required for the Minto coal tests. This coal has a low softening temperature and tended to clinker at the end of the feed tube into the combustor. This problem was largely overcome by pneumatically feeding the blended coal-limestone into the recycle line where it is diluted with recycle material prior to entering the combustion zone.

Because Minto coal has a high volatile content, feeding to the combustor could begin at 650°C. Best operation was obtained in the 850-880°C range with a feed rate of 5.5 kg/h blended coal-limestone feed (Ca/S=1.6) and a fluidizing velocity of 3.8 m/s.

Corrosion Probes

In order to acquire exposure time on the corrosion probes, only the time during which coke was being fed to the combustor was counted. In fact, the probes were exposed to the high temperatures and particle errosion for 30 - 40% longer time than the

125 h of coke feeding. Part of this extra time was due to difficulties with the unit, particularly in the early stages of the work, which resulted in some combustion runs of less than two hours. There were 33 startups but only 17 were of 4.5 h and longer. The probes were removed and replaced with new ones at the conclusion of the coke trials.

More operating experience and less combustor problems resulted in more efficient tests with the Minto coal than the Syncrude coke. There were 26 startups and 23 runs were of 4.5 h and longer.

Recovery of Vanadium and Nickel

Vanadium and nickel are valuable metals which, if they could be easily recovered from the ash, would enhance the economics of the fluidized bed combustion of coke. As will be shown later, both elements are concentrated in the baghouse ash although they are still much diluted with calcium compounds. The usual method of recovering vanadium from boiler and fly ashes involves a salt roast followed by a hot water or alkali leach. A series of roasts of 100 g baghouse ash blended with NaCl, Na_2CO_3 and a mixture of the two salts was carried out for four hours at 800°C. The calcine was leached with water in a stirred reactor at 95°C for three hours, followed by filtration and washing. The combined filtrate and wash was analysed for V and Ni. These results will be discussed later.

MATERIAL

SYNCRUDE LIMESTONE AND COKE

Limestone from an outcrop at Beaver Creek and Provincial Highway 963 near Fort McMurray was used in these tests. Fifty tonnes were quarried in March, 1983. For these combustion trials the limestone was crushed in a jaw crusher, a cone crusher and finally a hammer mill. It was sieved on a viabratory 35 mesh (500 um) screen. The size distribution is given in Figure 2. Unfortunately, it is much finer than desired, the D50 being about 13 um and D80 being 75 um. This fine size resulted in some inefficiency of limestone utilization as will be discussed later. The chemical analysis is given in Table 1.

Fifty tonnes of fluid petroleum coke were purchased from Syncrude Canada Ltd. at the same time as the limestone was acquired. The coke was sieved through a 20 mesh (850 um) screen to remove the occasional large piece which would cause problems in the pneumatic feeder.

One kg coke and 0.6 kg limestone were blended to give a Ca/S molar ratio = 2.0 in the feed to the combustor.

Table 1 - Analysis of Syncrude fluid coke and limestone

Syncrude Coke Proximate/Ultimate analysis (mass %, dry basis)	
Ash	6.68
Volatile matter	6.79
Fixed carbon (by diff)	86.53
Carbon	82.40
Hydrogen	1.43
Sulphur	6.96
Nitrogen	2.12
Ash	6.68
Oxygen (by diff)	0.41

Table 1 (con't) - Analysis of Syncrude fluid coke and limestone

Calorific value 29.5 MJ/Kg

Ash composition, mass %

SiO_2	41.3	TiO_2	3.6
Al_2O_3	25.1	NiO	1.2
Fe_2O_3	10.9	V_2O_5	4.7
Other oxides	14.1		

Fort McMurray limestone composition, mass %

SiO_2	13.56	MgO	0.0
Al_2O_3	3.31	SO_3	1.36
Fe_2O_3	1.43	Na_2O	0.0
TiO_2	0.34	K_2O	1.00
P_2O_5	0.14	BaO	0.10
CaO	41.23	SrO	0.02
LOI	35.15		

Of particular interest to this work is the analysis of vanadium and nickel in the coke. Most analytical techniques require the coke to be ashed or digested prior to the analysis of the elements in the ash. The method used by ERL is to ash the coke in a plasma at 750°C followed by analysis by inductive coupled plasma (ICP). In the analysis by MSL, the coke was analysed "as is" by emission spectroscopy. Ahlstrom uses atomic adsorption specroscopy (AAS) on the dissolved ash. The technique used by Syncrude (SC) is not known. These results are presented in Table 2.

Three samples from the Ahlstrom tests were analysed by Chemex Laboratory, Vancouver, by atomic adsorption spectroscopy, three additional samples were analysed by MSL by emission spectroscopy, and a further three analysed by ERL by ICP. The coke used in the Ahlstrom tests was composed of 30 t of the total 50 t purchased in March 1984 and an additional 20 t from a 1985 purchase. A comparison of the vanadium and nickel analysis is

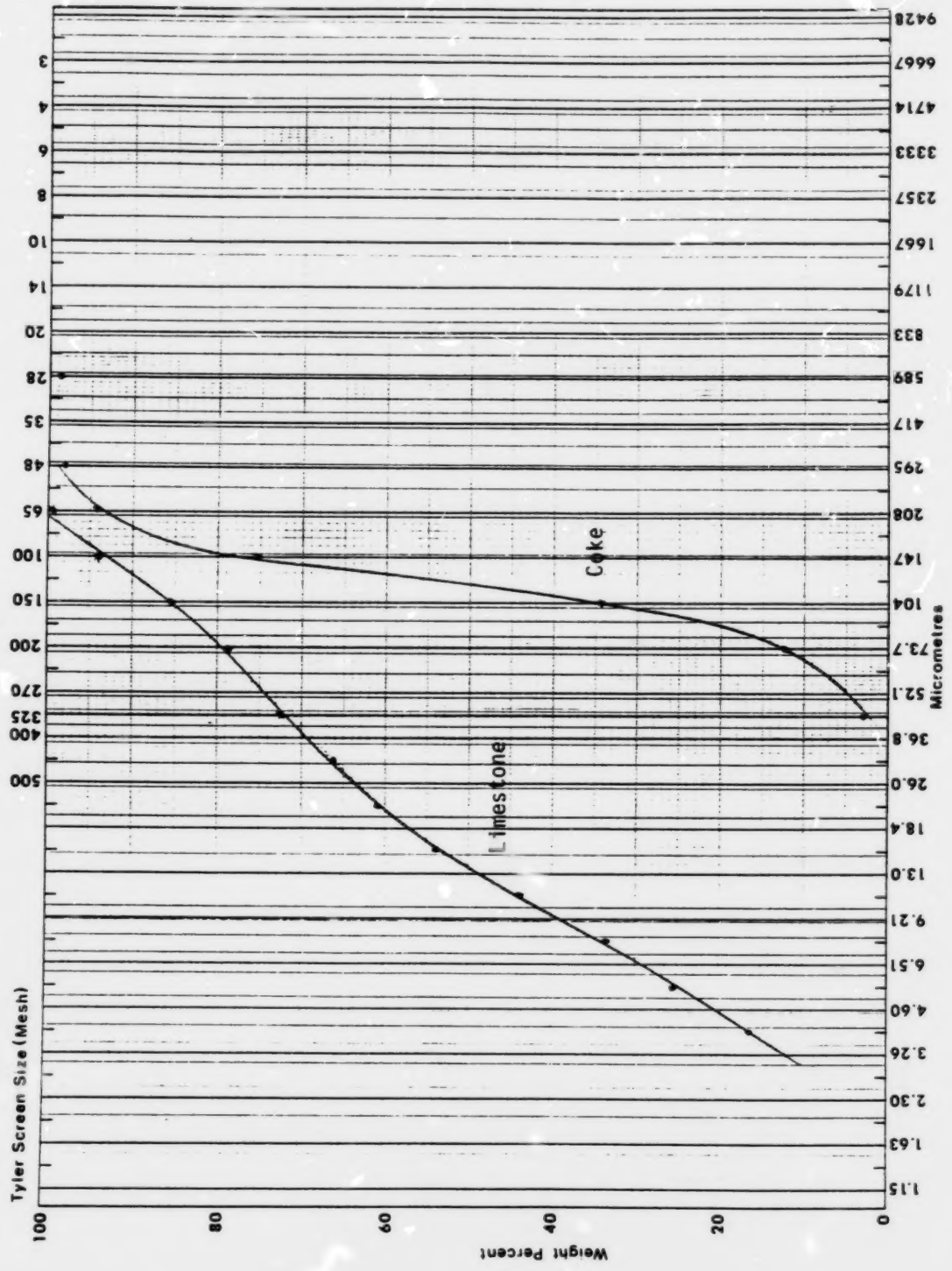


Fig. 2 - Particle size distribution of Syncrude coke and limestone

presented in Table 3. The values of V and Ni determined by Ahlstrom are considerably higher than those determined by the other laboratories. MSL's results appear to be low. The difficulty with all these data is determining which are accurate and which should be used for determining the metal balances. Average values derived from MSL, ERL and Chemex results were used in the material balances: V=0.135% and Ni=0.056%.

Table 2. Analysis of V and Ni in coke and ash. All different samples

Analyser	ERL(a)	ERL(b)	MSL(c)	SC(d)	Ahlstrom(e)
V_2O_5	3.83	4.7	-	3.7	3.9
NiO	1.51	1.23	-	1.3	0.9
% Ash (dry)	6.7	6.9	-	7.1	9.5
V in coke	0.143	0.182	0.110	0.147	0.207
Ni in coke	0.079	0.067	0.053	0.072	0.067

a) 1984 sample
b) 1985 sample from Queen's Univ tests
c) average of five samples
d) Heaton (1984), based on composite sample collected from production during two months in 1984
e) 1985 tests

Table 3. Analysis of V and Ni in coke samples

	Coke							
	MSL		Ahlstrom		Chemex		ERL	
Ahlstrom test no	V	Ni	V	Ni	V	Ni	V	Ni
#4	0.092	0.046	0.207	0.06	-	-	-	-
#11	0.130	0.053	0.198	0.73	-	-	-	-
#15	0.095	0.046	0.195	0.73	-	-	-	-
#8b	-	-	0.190	0.68	0.14	0.05	-	-
#14	-	-	0.200	0.72	0.13	0.05	-	-
#16	-	-	0.196	0.74	0.14	0.05	-	-
#10	-	-	0.192	0.73	-	-	0.15	0.06
#12	-	-	0.197	0.74	-	-	0.15	0.06
#14	-	-	0.194	0.72	-	-	0.16	0.06
MSL barrel								
#1	0.108	0.056						
#2	0.116	0.055						
#3	0.104	0.051						
#4	0.104	0.055						
#5	0.120	0.050						

New Brunswick Limestones and Minto Coal

One objective of the trials with Minto coal was to evaluate various sources and sizes of New Brunswick limestones for potential use in the Chatham CFBC. Two limestones were obtained from Elmtree Resources Ltd, one from their Petit Rocher quarry and the other from the Sormony quarry. Two samples were received from Havelock Lime Works Ltd; a barrel of Stastrong and a bag of Lime Dust. The analysis of material is given in Table 5. All limestones were sieved to remove any +1.68 mm particles as these large pieces could cause blockages in the pneumatic injector. Less than 1% of the Elmtree limestone was larger than this sieve, but about 3% of the Havelock Stastrong was rejected.

These various materials were tested with a Ca/S molar ratio of 1.6 and some with a ratio of 2.0. Additionally, material from Sormony was sieved through a 210 um screen and two parts of the undersize were blended with one part original material to produce a limestone with a finer size distribution. Some Stastrong material was slurried with water and decanted in order to remove some of the very finely sized particles. After drying the resultant "deslimed" Stastrong had a similar size distribution to the Elmtree limestones. The size distribution of all New Brunswick samples are given in Figure 3.

The Minto coal was acquired from stock at CCRL. It was ground, sieved to -1.68 mm and dried in shallow pans over steam heated radiators. The analysis of the coal and limestones are given in Table 4.

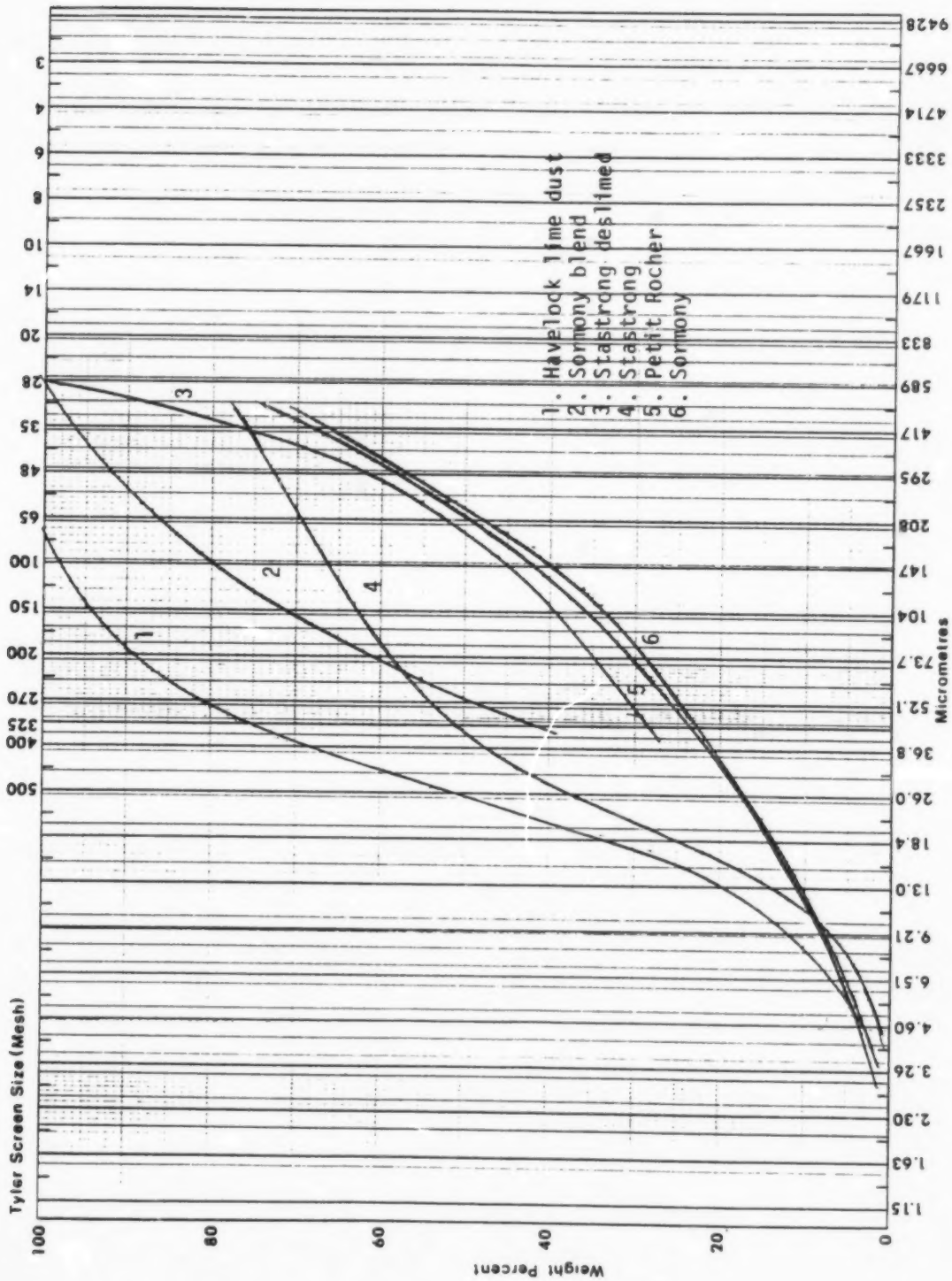


Fig. 3 - Particle size distribution of New Brunswick limestones

Table 4. Analysis of Minto coal and New Brunswick limestones

Proximate/Ultimate Analysis
(mass %, dry basis)

	QAFBC(7)	Stover	ERL
Ash	17.4	22.0	15.62 (a)
Volatile matter	33.7	30.7	34.84 (a)
Fixed carbon (by diff)	49.3	47.3	49.54 (a)
Carbon	68.3	62.6	
Hydrogen	4.1	4.3	
Sulphur	7.4	9.0	6.82 (b)
Nitrogen	0.8	0.8	
Oxygen (by diff)	2.4	1.3	

(a) average of 7 samples from these combustion trials
(b) average of 16 samples from these trials (standard deviation 0.19)

Calorific value, dry, MJ/kg 34.6 27.4

Ash composition, mass % (ERL, 1986)

SiO_2	28.4	CaO	4.7
Al_2O_3	9.7	MgO	0.2
Fe_2O_3	47.4	SO_3	4.1
TiO_2	0.5	Na_2O	0.2
P_2O_5	1.6	K_2O	0.4

Composition of New Brunswick limestones

	Havelock			Elmtree		
	(Hamer 11)	ERL	MSL(a)	(Hamer)		MSL(a)
				Petit Roche		Sormony
$CaCO_3$	94.6	98.8	101.2	91.5	93.5	91.4
$MgCO_3$	1.8	0.7		1.0		
Fe_2O_3	0.4	0.2		0.6		
Al_2O_3	1.4	0.2		1.5		
SiO_2	3.1	1.3		7.0		
Na_2O	0.03	-		0.04		
K_2O	0.2	-		0.2		

(a) average of two samples from this combustion series

RESULTS

SYNCRUDE COKE RUNS

After the initial shakedown trials with Syncrude coke, the basic CFBC operating parameters were determined and kept reasonably constant thereafter. Table 5 summarizes the latter series

of runs for which detailed data were collected and samples were taken for analysis. The feed was a blend of coke and limestone in a Ca/S ratio of 2.0. The excess air and the SO_2 capture are calculated from the gas analyses after steady state conditions were reached.

Table 5. Process data and SO_2 reduction

Run no	Feed kg/h	velocity m/s	XS air %	Mean temp C	SO_2 ppm	SO_2 % capture
010486	5.03	3.5	21	830	435	91
020486	4.74	3.1	10	850	470	91
030486	5.13	3.3	8	850	368	93
040486	5.14	3.4	13	844	332	94
080486	5.17	3.3	7	845	710	87
090486	4.62	3.1	13	846	550	89
110486	5.09	3.3	7	853	630	89
220486	4.61	3.4	14	860	440	91
230486	4.77	3.2	10	850	630	88
240486	4.68	3.1	11	850	600	89
250486	4.65	3.1	10	870	350	93
120586	4.86	3.4	17	852	322	94
140586	5.07	3.4	10	860	300	94
150586	5.20	3.2	5	870	280	95
160586	5.34	3.2	8	872	240	96
average					444	92%

Thermogravimetric Analysis of Ash

Ash samples from several of these runs were examined by TG/DT to evaluate the composition of the ashes and the efficiency of the combustor. This method, devised by Mikhail (12) can distinguish between fuel carbon and carbon contained in uncalcined limestone. As this is a lengthy procedure, only a few samples were analysed, the results of which are given in Table 6.

Table 6. TG/DT analyses of ash samples

Run	%$CaCO_3$			%C			%$CaSO_4$	
	FB	HX	BH	FB	HX	BH	FB	HX
170286	-	-	13.8	-	-	6.0	-	-
010486	1.5	11.4	-	0.18	14.9	-	40.9	31.7
020486	1.6	-	17.3	0.2	-	3.0	43.8	-
030486	2.7	-	-	0.45	-	-	52.3	-
040486	0.9	11.4	22.8	-	12.0	6.0	-	-
080486	3.1	-	-	1.07	-	-	54.2	-
090486	3.0	-	-	0.86	-	-	57.4	-
160586	-	4.8	10.2	-	12.0	3.0	-	-

FB = fluidized bed ash, HX = heat exchanger ash, BH = baghouse ash

The bed material contains an average of 2.1% unreacted limestone and 0.5% uncombusted carbon. There is some variation in the calculated sulphated lime. The heat exchanger ash averages 9% $CaCO_3$ and 13% C. The baghouse ash averages 16% $CaCO_3$ and 4.5% C. The high values of unreacted limestone are a reflection of the very small particle size of the feed material. The combustion efficiency for 040486, which is the only run for which complete TG/DT analysis was done, was calculated as 96.5%.

Material Balance

As the bed, heat exchanger and baghouse were drained at the completion of each run, accurate weights of the ash streams were determined. A mass balance, given as Appendix A, was calculated on the assumption of complete combustion of the fuel and calcination of the limestone. The theoretical ash is 29.73% for the coke:limestone feed ratio of 1:0.6 assuming complete combustion and calcination. The ash content of the coal used for start-up is 11.10%. The collected ash mass was then corrected for incomplete combustion and calcination by assuming that the heat exchange ash contained 9% $CaCO_3$ and 13% C and the baghouse ash

contained 16% $CaCO_3$ and 5% C. No correction was made for the small amount of unreacted material in the bed ash. Further correction was made for the weight gain due to the oxidation of sulphur to form $CaSO_4$.

On the basis of the above assumptions, the average accountability of material, that is, mass in/mass out is 103.1% with a standard deviation of 3.8% for 14 trials. As more than one half of the run balances exceed 100%, it is probable that the corrections due to incomplete combustion of carbon and unreacted limestone were insufficient.

Calcium, Sulphur, Vanadium, and Nickel Balances

The ash streams from 15 runs were chemically analysed for Ca, S, V, and Ni. Carbon was determined for some samples by TG. In some of the trials the heat exchanger and baghouse were emptied halfway through and again at the end of the run. The second sample should be closer to steady state conditions. The ash analyses are given in the three tables of Appendix B.

The highest values for calcium and sulphur and the lowest values for vanadium and nickel occur in the bed material (averages: Ca = 25.14%, S = 13.21%, V = 0.10% and Ni = 0.04%). The calcium content is similar in the heat exchanger and baghouse, (Ca = 21.06% and 20.97 %) but the sulphur decreases as the particle size decreases from the heat exchanger to baghouse (S = 8.19% and 5.12%). The concentrations of both heavy metals increase with decreasing particle size so that the highest concentrations are in the baghouse (V = 0.28% and Ni = 0.14%).

As a matter of interest, these data were compared to the average ash analyses of the two tests in the Ahlstrom trials (AC) whose Ca/S ratio was closest to 2.0 , that is, Test 7A (Ca/S = 2.11) and Test 11 (Ca/S = 1.76)(ref 2). The analysis for calcium and sulphur for the two systems are quite close as seen in Table 7. The metal analyses are in poor agreement, especially for the baghouse ash.

Table 7. - Comparison of ash analysis from Ahlstrom and MSL pilot-scale CFBC

Element	Bed		Boiler		Baghouse	
	AC	MSL	AC	MSL	AC	MSL
Ca %	23.6	25.1	21.0	21.1	20.5	21.0
S %	11.0	13.2	7.90	8.19	6.50	5.12
V %	0.067	0.095	0.29	0.12	0.73	0.28
Ni %	0.013	0.042	0.13	0.06	0.24	0.14

By combining the mass of the ash streams, given in Appendix A, and the chemical analyses, Appendix B, the element balance for Ca, S, V and Ni were calculated and given in the following Tables 8,9,10, and 11.

The calcium balance, at 90.9% recovery, is not as good as would be expected. As there should be essentially no loss of calcium from the system, the accountability should be higher. Limestone samples were not analysed for each run so some error could occur for that reason.

Table 8. Calcium balance, g (Ca in feed = 17.66%)

	In			Out				
Run	Bed	Feed	Total	Bed	HX	BH	Total	% Out/In
010486	1326	2258	3584	1559	834	813	3206	89.4
020486	1373	2320	3693	1808	1688	690	3286	89.0
030486	1485	2873	4345	2115	1389	869	4373	100.6
040486	1662	2553	4215	2073	1013	723	3809	90.4
080486	1723	4015	5738	2345	1529	1264	5138	89.5
090486	1887	2528	4415	2190	1062	791	4043	91.6
110486	1735	2810	4545	2201	965	907	4073	89.6
220486	2002	2547	4549	2663	732	749	4144	91.1
230486	1861	2634	4495	2804	588	740	4132	91.9
240486	1989	3011	5000	2763	906	978	4647	92.9
250486	1874	2973	4847	2509	951	856	4316	89.0
120586	1844	3023	4867	1355*	1082	874	3311	-
140586	1884	2798	4682	1901	1374	1016	4291	91.6
150586	1919	2873	4792	2206	938	994	4138	86.3
160586	1799	3245	5044	2244	1348	929	4521	89.6
						Mean		90.9
						Std Dev		3.2
Distribution in ash, %				52.2	27.3	20.5		

* Some material was lost from the 120586 bed material

The average sulphur accountability of 90.7% is essentially the same as for the calcium. The sulphur retention based on the gas analysis during steady state operations averaged 92% for this series of runs. Almost two thirds of the sulphur is captured in the bed material, and about one quarter in the heat exchanger ash.

The accountability of vanadium is 93% and of nickel is 106%. The balances are based on using a value of 0.135% for the vanadium and of 0.056% for the nickel in the coke. A relatively small difference in these analytical values has a large effect on the balances. For example, if the value for nickel were taken as 0.066%, which is the average of Ahlstrom's analysis for this element, rather than the average of the MSL, ERL, and Chemex data, the accountability of nickel would also be 93%. Both

metals concentrate in the baghouse ash with about 45% of the total.

Table 9. Sulphur balance, g (S in feed = 6.90%)

	In			Out				
Run	Bed	Feed	Total	Bed	HX	BH	Total	% Out/In
010486	654	893	1547	762	279	177	1218	78.7
020486	671	918	1589	924	299	195	1418	89.2
030486	759	1132	1891	1141	529	219	1889	99.9
040486	897	1011	1908	1155	399	192	1746	91.5
080486	960	1587	2547	1167	609	299	2075	81.5
090486	939	1000	1939	1223	432	187	1842	95.0
110486	969	1113	2082	1227	437	269	1933	92.8
220486	1051	1011	1762	1341	284	173	1798	102.0
230486	937	1043	1980	1367	203	180	1750	88.4
240486	970	1189	2159	1412	331	210	1953	90.4
250486	958	1175	2133	1269	398	213	1880	88.1
120586	988	1197	2185	750*	486	216	1452	-
140586	965	1108	2073	981	575	220	1776	85.7
150586	990	1130	2130	1166	442	269	1877	88.1
160586	951	1281	2232	1253	656	274	2185	97.9
						Mean		90.7
						Std Dev		6.6
Distribution in ash, %				64.6	23.2	12.2		

* Some material was lost from the 120586 bed material

Table 10. Vanadium balance, g (V in feed = 0.0844%)

	In			Out				
Run	Bed	Feed	Total	Bed	HX	BH	Total	% Out/In
010486	6.4	17.2	23.6	6.4	4.2	9.3	19.9	83.7
020486	5.6	17.7	23.3	6.8	4.6	7.0	18.4	79.1
030486	5.6	21.9	27.5	9.8	7.9	12.0	29.7	107.8
040486	7.7	19.5	27.2	7.6	4.9	9.2	21.7	79.6
080486	6.3	30.7	37.0	7.0	8.4	16.4	31.8	85.7
090486	5.6	19.3	24.9	8.0	6.1	10.2	24.3	97.5
110486	6.3	21.5	27.8	8.1	5.8	12.4	26.3	94.7
220486	8.4	19.3	27.7	13.0	5.1	9.4	27.5	99.4
230486	9.1	20.1	29.2	9.9	3.7	10.0	23.6	80.6
240486	7.0	23.0	30.0	12.4	6.1	11.7	30.3	101.0
250486	8.4	22.7	31.1	10.2	6.7	12.8	29.7	95.5
120586	6.3	23.4	29.4	4.2*	6.4	12.5	23.1	-
140586	5.6	21.4	30.0	4.9	7.0	13.0	24.9	99.2
150586	4.9	21.9	26.8	7.7	5.8	14.2	27.7	103.3
160586	6.3	24.8	31.1	6.9	7.6	15.5	30.0	96.3
						Mean		93.1
						Std Dev		9.5
Distribution in ash, %				32.5	22.6	44.8		

* Some material was lost from the 120586 bed material

Table 11. Nickel balance, g (Ni in feed = 0.0350%)

	In			Out				
Run	Bed	Feed	Total	Bed	HX	BH	Total	% Out/In
010486	4.3	7.2	11.5	3.2	2.1	5.0	10.3	89.9
020486	2.8	7.4	10.2	5.1	2.7	3.8	11.6	113.8
030486	4.2	9.1	13.3	3.6	4.2	6.4	14.2	106.7
040486	2.8	8.1	10.9	3.4	2.7	5.2	11.3	102.7
080486	2.8	12.7	15.5	4.3	4.9	8.2	17.4	112.1
090486	3.5	8.0	11.5	5.3	3.1	5.1	13.5	117.0
110486	4.2	8.9	13.1	4.5	2.9	6.7	14.1	107.4
220486	3.5	8.1	11.6	5.0	2.6	4.9	12.5	107.5
230486	3.5	8.4	11.9	4.0	1.9	5.3	11.2	94.2
240486	2.8	9.6	12.4	4.1	3.0	6.0	13.1	105.8
250486	2.8	9.4	12.2	3.7	2.8	6.5	13.0	106.4
120586	2.1	9.6	11.7	1.1*	3.2	6.1	10.4	-
140586	2.1	8.9	11.0	2.1	3.0	6.0	11.1	101.1
150586	2.1	9.1	11.2	2.6	2.6	6.7	11.9	105.9
160586	2.1	10.3	12.4	2.6	3.3	7.6	13.5	109.1

						Mean		105.6
						Std Dev		7.1
Distribution in ash, %				29.9	23.4	46.7		

* Some material was lost from the 120586 bed material

Fate of Vanadium

In petroleum coke, vanadium and nickel exist as complex porphyrins. During combustion, the vanadium reportedly volatalizes into the gas phase as oxides and hydroxides (10). Although it is suggested that the vanadium will be lost into the gas phase, an examinaton of the ash shows vanadium to be present. Samples of coke ashed at 700, 850 and 950^{o}C in a muffle furnace were examined by ESCA. This technique analyses the surface 2 nm or so. Photomicrographs of the ash show a decrease in the ash particle volume with increasing temperature, Figures 4 and 5. All of the samples contained 11-16% carbon which indicates incomplete combustion.

A comparison of the bulk sample analysis and ESCA are presented in Table 12. The later results indicate that at the

Fig. 4 - Ash particles of coke combusted at 700°C

Fig. 5 - Ash particles of coke combusted at 1000°C

higher temperatures, the vanadium, in the form of pentoxide, concentrates near the surface of the ash particle whereas the sodium appears to be depleted near the surface. There was insufficent nickel for the ESCA to detect although titanium did show up well and follows the same trend as the vanadium. Thus, contrary to the literature, the vanadium does not appear to have volatalized as a gas phase.

Table 12. Analysis of coke ashed in a muffle furnace

Ashing Temperature	Bulk Analysis		ESCA Analysis		
	V	Na	V	Ti	Na
700°C	2.32	1.36	1.0	tr	0.5
850°C	2.85	1.59	4.6	0.8	0.6
950°C			5.0	1.2	0.6

FACT Evaluation of the Ca-Mg-Na-V--Ni-S-O-C System

The Facility for the Analysis of Chemical Thermodynamics (FACT) system was used to determinine the fate of vanadium in the combustor according to thermodynamic data. The reactions were determined in the temperature range 700 - 950°C. The first system studied assumed the combustion of the coke with a 10% excess of oxygen and no limestone present. The second system assumed a limestone addition with a Ca/S molar ratio = 1.7. The mole ratio of the elements in the systems are specified in Table 13.

Table 13. Composition of Ca-Mg-Na-V-Ni-S-O-C Systems, moles

Elements	System 1	System 2
Ca	0.37	25
Mg	0.31	2.7
Na	0.22	0.4
V	0.39	0.27
Ni	0.10	0.07
S	21.25	14.5
C	650	443
O	2000	1500

In the first system all the magnesium reacted with vanadium to form $MgO.2V_2O_5$ while the small amount of remaining vanadium reacted with calcium to form $CaO.V_2O_5$. The remaining calcium reacted with sulphur to give $CaSO_4$. The nickel oxidized to NiO and the sodium sulphated to Na_2SO_4, liquid or solid depending on the temperature, in both systems. In the second system with limestone addition, all of the vanadium reacted as $CaO.3V_2O_5$. The magnesium simply formed MgO. The remaining calcium was essentially present as $CaSO_4$ and CaO. Thus, based on thermodynamics, the vanadium reacts completely with magnesium or calcium, depending upon whether an excess of lime is present, to form stable solid compounds.

Roast - Leach of Baghouse Ash

Vanadium and nickel are valuable metals that concentrate in the baghouse ash, although they are much diluted with calcium compounds. As given in Appendix B (Table B3) the average V = 0.28, Ni = 0.14 and Ca = 21.0%. The high calcium values essentially preclude the use of acid leaches. A four-hour, hot water leach did not liberate any vanadium or nickel. Roasts with NaCl, Na_2CO_3 and a blend of the two, followed by a hot water

leach did extract some vanadium but negligible nickel as shown in Table 14.

Table 14. Extraction of V and Ni from a 4h, 800C, salt - roast and water leach of 100 g baghouse ash

Additive	% V extraction	% Ni extraction
10 g NaCl	0.26 %	0.10 %
10 g Na_2CO_3	2.14	0.11
25 g NaCl	0.75	0.22
25 g Na_2CO_3	23.9	0.12
10 g NaCl + 10 g Na_2CO_3	1.04	0.19

The best roast was with 25 g Na_2CO_3 which resulted in 24% V extraction. However, the actual quantity of V liberated was only 0.067 g which would have a value of about one-tenth of the value of the soda ash required to liberate it. In view of these rather discouraging results no further tests were made to recover the heavy metal content of the ash. Etsell (13) confirmed that vanadium was much more difficult to recover from coke ash when the coke had been combusted in the presence of lime compared to ash with no lime present. This is probably due to the formation of a stable calcium vanadate compound.

MINTO COAL RUNS

A series of combustion trials were conducted with Minto coal and two limestones from Elmtree (Sormony and Petit Rocher) and a limestone (Stastrong) and lime dust from Havelock. The Ca/S ratio was 1.6 and 2.0 and the mean limestone sizes, shown in Figure 5, were approximately 50 um and 200 um. Table 15 summarizes the series of tests. The SO_2 values represent steady state conditions achieved after 2 - 3 turnovers of the bed.

Table 15. Minto coal trials

Run	Limestone	Size um	Ca/S	Feed kg/h	Vel m/s	% XS air	mean temp	SO_2 ppm	SO_2 retn
860902	none		0	3.47	3.6	15	824	5920	5
860918	Sorm	220	1.6	5.49	3.4	16	ns	3068	50
860919				5.48	3.4	20	ns	3140	51
860925				5.06	3.6	16	ns	2300	63
861028				5.70	3.5	11	851	1894	71
861110				5.65	3.4	13	870	2590	59
861029		220	2.0	4.87	3.5	30	880	1330	75
861030				5.15	3.4	25	871	1355	77
861008		55	1.6	5.20	3.6	15	846	2206	65
861016				5.12	3.6	10	825	2185	66
861001	P Roch	210	1.6	5.33	3.6	12	859	1860	71
861002				5.22	3.6	13	838	2080	67
861112				4.90	3.4	23	861	2140	63
861113		210	2.0	6.36	3.4	26	869	1750	69
860929	Stas	44	1.6	5.13	3.6	11	839	1952	71
860930				4.78	3.8	18	881	1523	75
861106				5.11	3.4	26	867	2715	52
861031		44	2.0	6.01	3.7	30	885	2484	55
861103				6.03	3.5	12	872	2365	63
861107		200	1.6	6.10	3.5	21	869	2265	62
861114				4.49	3.1	30	862	2115	61
861017	L dust	25	1.6	5.25	3.5	17	849	2683	56
861020				5.31	3.1	8	ns	3290	50

Sorm = Sormony, P Roch = Petit Rocher, Stas = Havelock Stastrong, L dust = Havelock Lime Dust
ns - not saved, computer difficulties

Ash Analysis

The ash streams were analysed for Ca, S and sulphate S. The samples taken during steady state conditions from the heat exchanger (HX2) and baghouse (BH2) were also analysed for total C and CO_2 from uncalcined $CaCO_3$. A comparison of some of the chemical analytical results with TG analysis of ashes gave reasonable agreement for C, and CO_2 but very poor agreement for sulphate S. Table 16 presents some TG data and the comparable chemical analysis. Appendix C gives the chemical analysis of the bed, heat exchanger and baghouse ashes. The sulphate S is not included.

From the chemical analysis and the masses of the various ash streams, the calcium and sulphur balance can be determined. The SO_2 capture calculated from the gas analysis is also given. The fuel carbon utilization is calculated after subtracting the carbon associated with the unreacted limestone. The summary of the tests for which analyses were done is given in Table 17.

Table 16. Comparison of TG/DT and chemical analysis of ash

Run	Ash	Method	%$CaCO_3$	%C	%$CaSO_4$
860925	FB	TG	4.5	0.2	44.7
		Chem	-	-	37.6
861028	FB	TG	15.9	0.0	46.4
		Chem	-	-	33.8
861114	FB	TG	7.5	0.0	50.6
		Chem	-	-	33.1
860925	HX	TG	10.2	20.5	25.5
		Chem	-	-	11.7
861030	HX2	TG	8.7	21.2	28.1
		Chem	9.0	11.5	11.0
861114	HX2	TG	20.9	11.9	31.5
		Chem	16.5	10.4	11.4
860925	BH	TG	11.4	31.0	24.5
		Chem	-	-	10.2
861030	BH2	TG	12.5	26.0	27.7
		Chem	11.1	23.6	12.9
861114	BH2	TG	13.7	27.0	28.1
		Chem	10.8	24.7	11.0

Table 17. Ca and S capture, combustion efficiency, % calcination

Run	Limestone	Ca/S	Ca %	S %	SO2(g) %	C util %	$CaCO_3$ % calcined
860929	Stastrong	1.6	97.3	72.0	71	88.5	74.3
860930	"	"	90.8	63.7	75	89.6	77.8
861001	P Rocher	"	102.5	74.1	71	88.0	81.7
861002	"	"	107.8	83.5	67	87.7	83.0
861008	Sormony F	"	82.7	57.0	65	83.8	66.1
861016	"	"	77.9	57.8	66	88.0	82.1
861017	H Dust	"	88.4	57.3	56	88.5	61.1
861020	"		96.2	60.2	50	89.3	61.5
861028	Sormony	"	103.5	78.7	71	87.4	89.3
861030	"	2.0	93.4	76.1	77	89.9	88.9
861103	Stastrong	"	97.2	64.5	63	89.2	71.7
861106	"	1.6	94.7	67.7	52	83.5	58.7

Table 17 (con't). Ca and S capture, combustion efficiency, % calcination

Run	Limestone	Ca/S	Ca	S	SO2(g)	C util	$CaCO_3$
861107	" C	"	97.2	71.2	62	90.0	85.6
861110	Sormony	"	116.0	65.8	59	85.2	82.4
861112	P Rocher	"	94.5	64.9	63	89.2	91.4
861113	"	2.0	95.5	71.7	69	86.3	90.6
861114	Stastrong C	"	96.9	75.3	61	88.7	80.9
Mean			96.0			87.8	
s.d.			8.8			2.0	

Sormony F = Sormony blend, Stastrong C = deslimed Stastrong

Although the average accountability of Ca, 96%, was somewhat better than in the Syncrude tests, the standard deviation was three times greater, indicating a less accurate material balance or that some change in the operating characteristics may have occurred. The total sulphur captured as determined by chemical analysis is generally higher than the SO_2 capture based on gas analyses. The combustion efficiency, based on the carbon balance, is quite reproducable at 88% (s.d. 2.0). This is a rather poor performance for a CFBC.

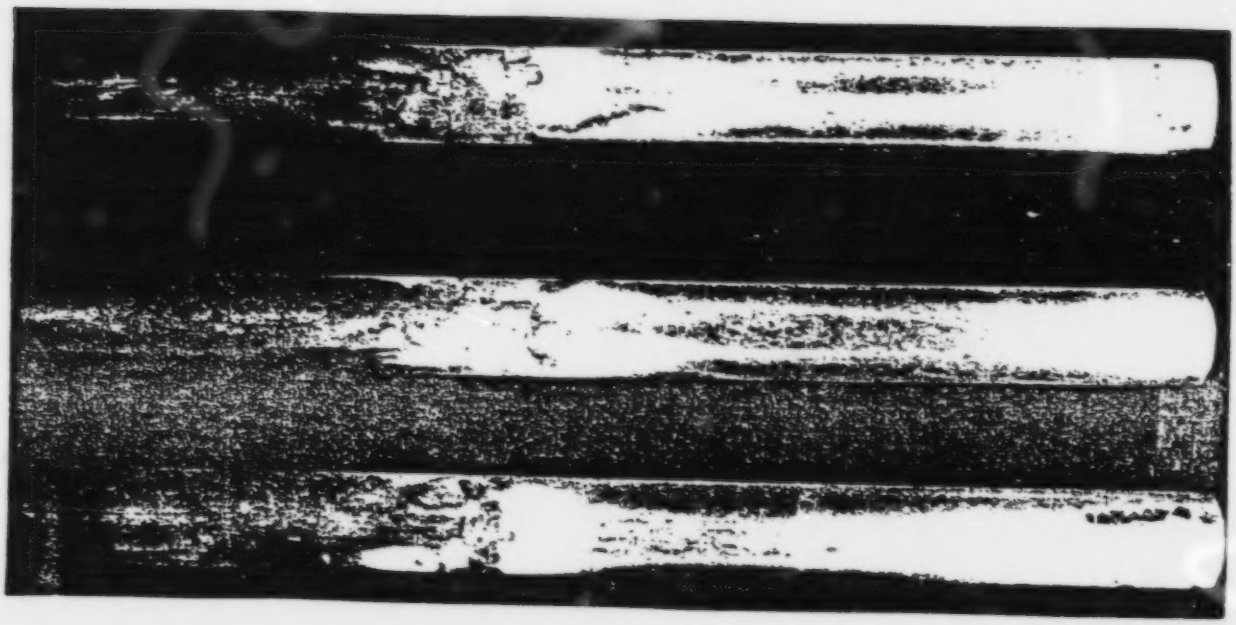
In general, approximately 25% of the "as received" Stastrong limestone passed through the combustor into the heat exchanger and baghouse without calcining. In the case of Havelock Lime Dust, the uncalcined portion is 40%. The Sormony and Petit Rocher had uncalcined portions of about 15%. The percentage of uncalcined limestone reflects the quantity of very fine particle sized material in the limestones. From the size distribution curves of Figure 3 and the percentage of uncalcined material for each limestone, the uncalcined portion corresponds approximately to the minus 20 um fraction.

The sulphur capture capacity of the New Brunswick limestones was not as effective as the Fort McMurray limestone. There was some inconsistancy in repetative tests with the same limestone as indicated in Table 17. With a Ca/S molar ratio = 1.6, the three "as received" limestones captured 65-70% SO_2. Lime dust captured about 55% SO_2. When the Ca/S molar ratio was increased to 2.0, the SO_2 capture for the two Elmtree limestones increased to 70-75%, but did not appear to improve for the Stastrong limestone. The effectiveness of the Stastrong in capturing SO_2 was similar for the tests with 44 um and 200 um material. This may be due to the loss of the finer fractions through the cyclone before they react. The finer sized Sormony limestone was less effective then the coarser "as received" material presumably for the same reason. As there was no apparent significant difference in SO_2 capture efficiency for the three limestones, the recommendation was made to use either of the Elmtree limestones, those deposits being closer to Chatham and hence less expensive than Havelock Stastrong.

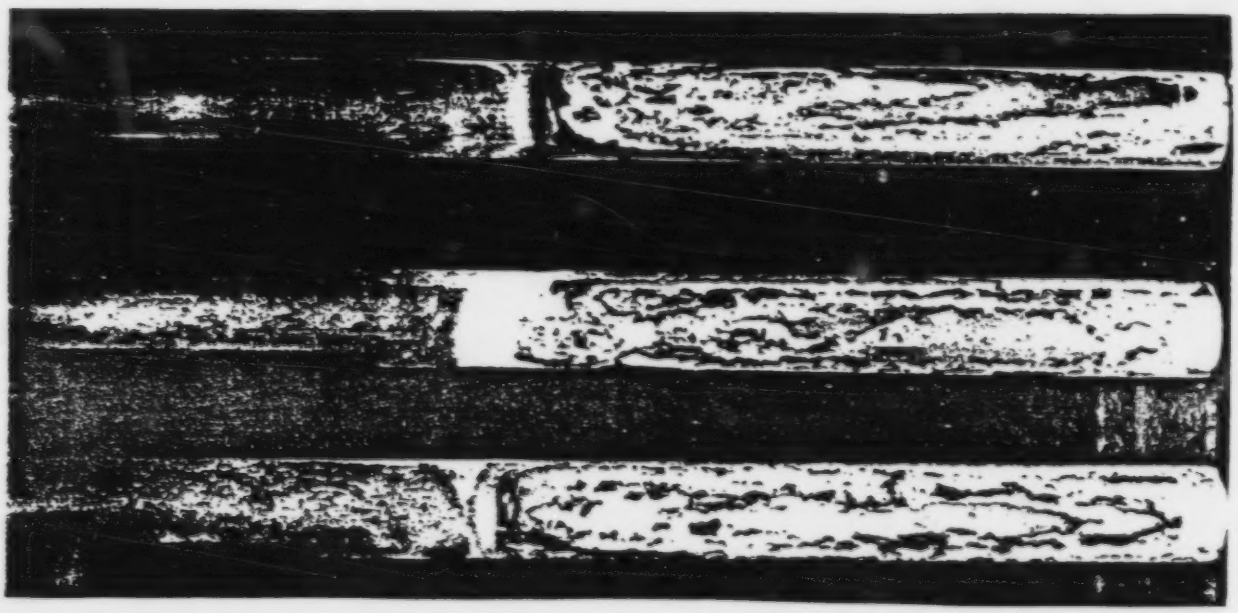
EVALUATION OF CORROSION PROBES

MINERALOGICAL EXAMINATION OF SCALE

Deposits on the bottoms of the metal probes in the combustor are shown in Figures 6 and 7. Upon cooling, some of the scale spalled off. As the combustor was operated only during the day the probes were subject to many cycles of heating and cooling. A sample of scale was collected by removing a hot probe, placing it

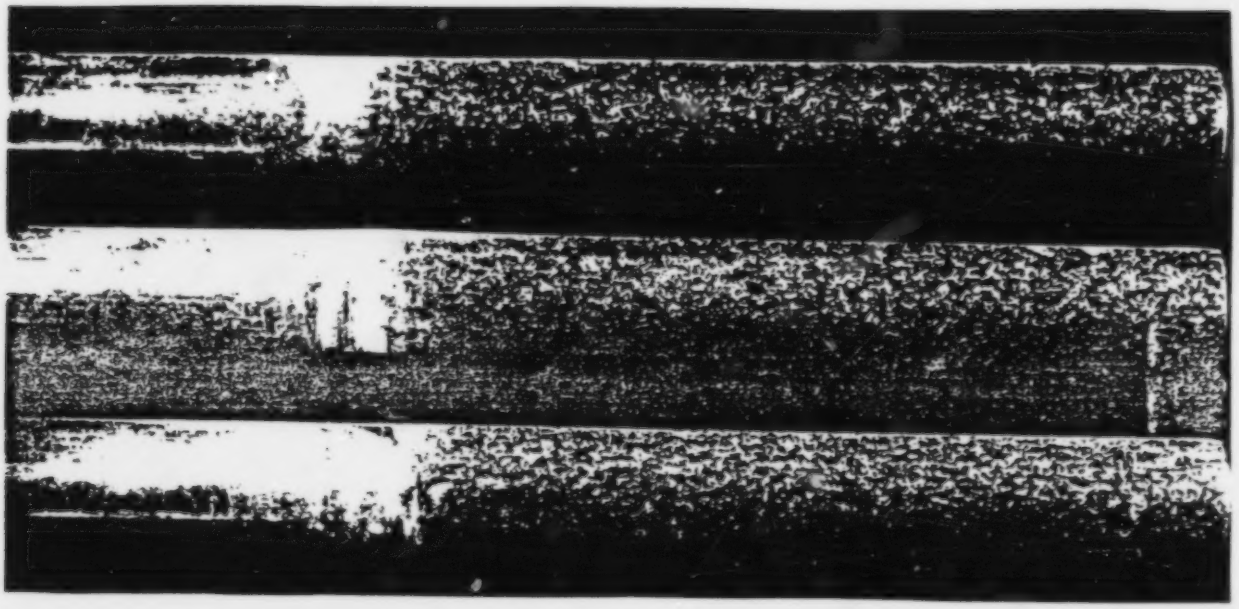


Tops of probes

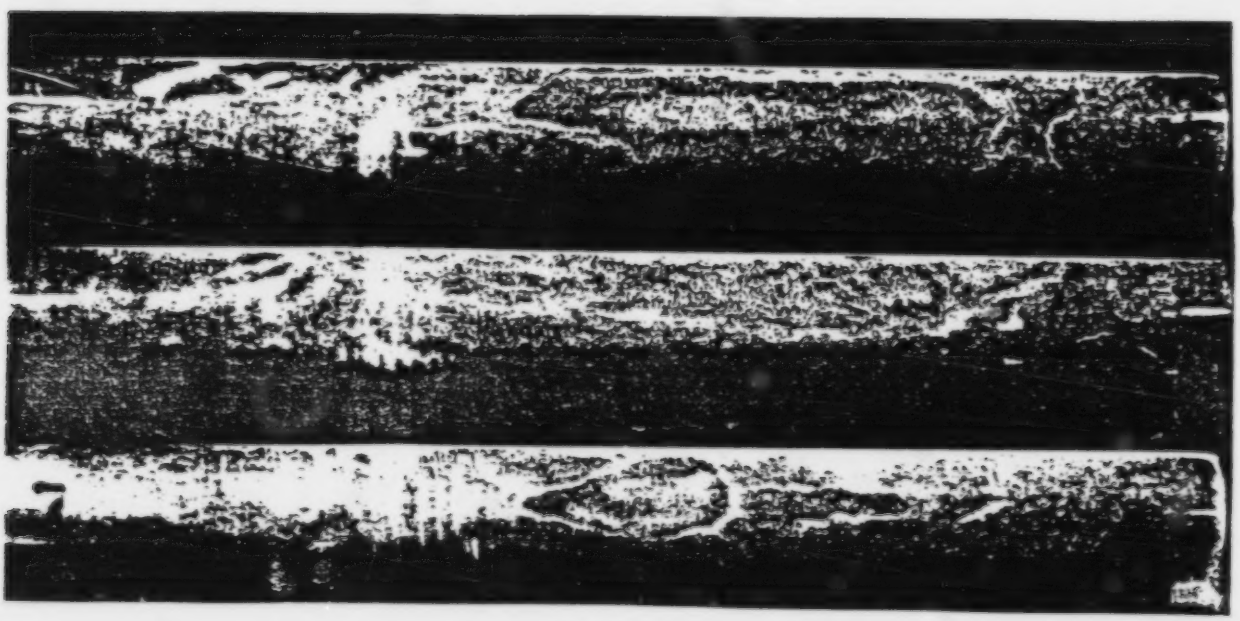


Bottoms of probes

Fig. 6 - Photographs of the tops and bottoms of probes from the Syncrude runs



Tops of probes



Bottoms of probes

Fig. 7 - Photographs of the tops and bottoms of probes from the Minto runs

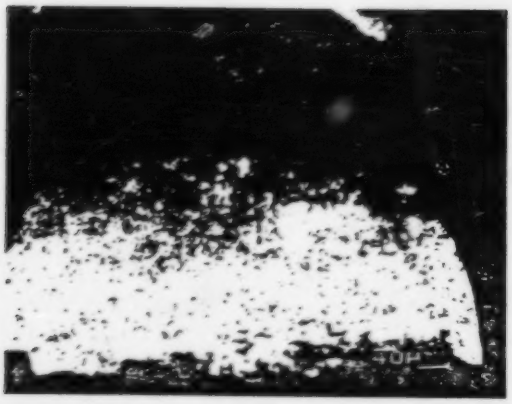
in a jar and recovering the flakes of scale as the probe cooled. The scale could be separated into a magnetic and a non-magnetic fraction. The former appeared to have spalled off the metal surface and the later appeared to be a layer flaked off from the scale itself. Samples were mounted, polished and examined by the Process Mineralogy Section of MSL using an electron probe micro-analyser.

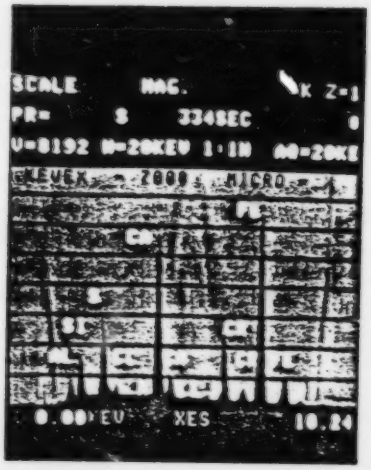
Figure 8 shows a photomicrograph of a flake of magnetic scale and an X-RAY scan (XES) of potential elements. The concentration maps for the major elements are Ca, Fe, S, and Cr are also shown. A scan for V did not show any measureable amount. The exterior of the scale appeared to be principally Ca and S. The iron layer appeared much wider than the Cr which is concentrated closest to the metal surface.

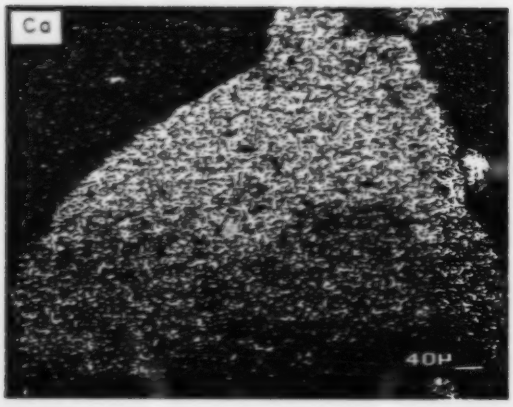
Figure 9 shows a photomicrograph of non-magnetic scale particles and an XES scan of the same area. The major elements present are Ca, S, and Si and, as the concentration maps show, all three appear to be evenly distributed throughout the particles of scale. The Ca and S are a perfect match. Essentially no V nor Ni was detected.

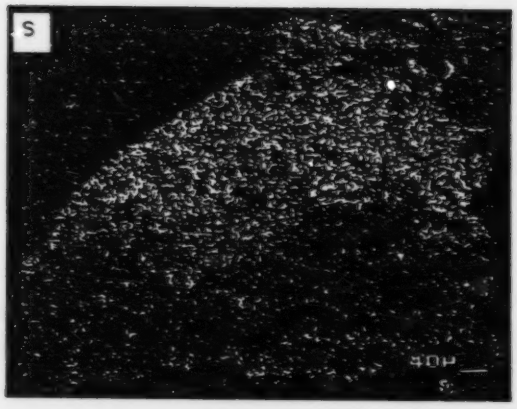
Chemical Analysis of Scale

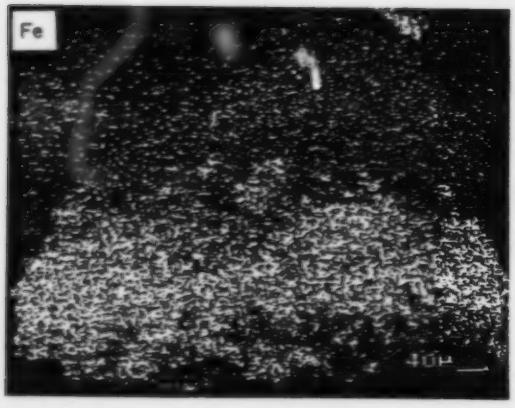
Chemical analyses of samples of scale are given in Table 18. The quantity of material from the thermocouple sheaths was separated into magnetic and non-magnetic fractions but there was insufficient material for complete analysis. Both the probe and thermocouple sheath are type 304 SS.











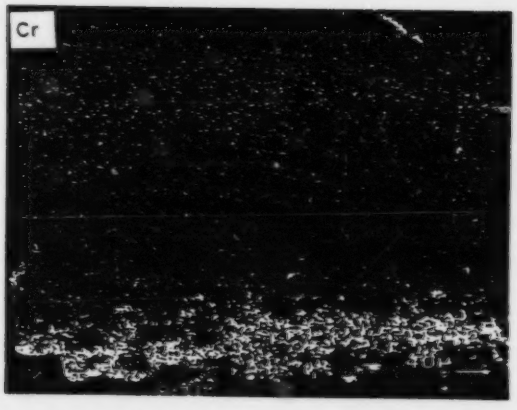
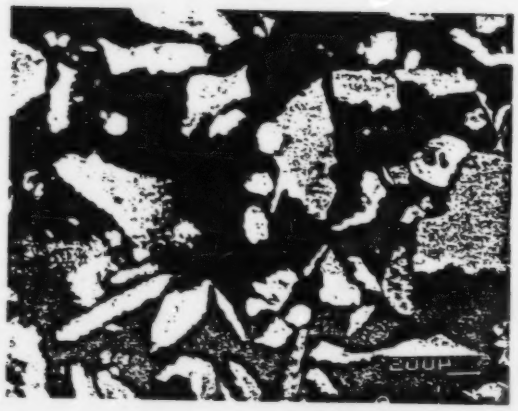
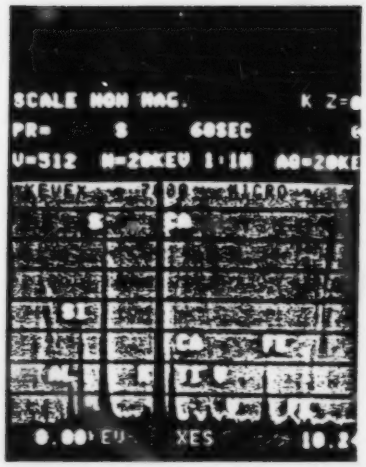
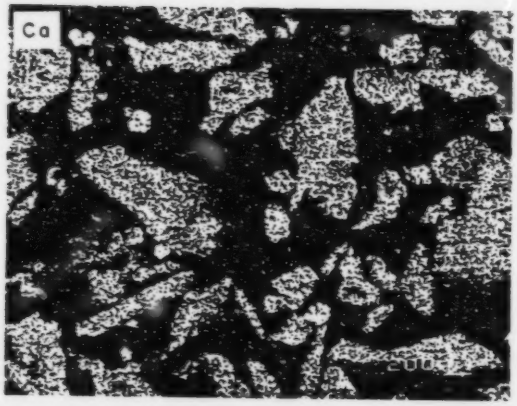
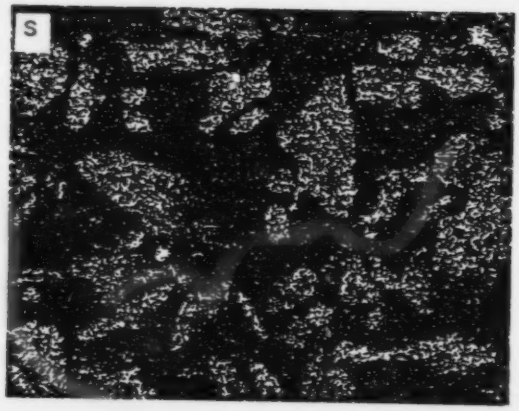


Fig. 8 - Photomicrographs of magnetic scale and X-ray scan of elements









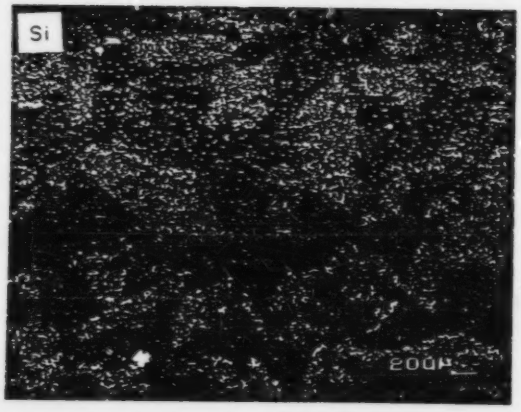


Fig. 9 - Photomicrographs of non-magnetic scale and X-ray scan of elements

Table 18. Analysis of scale, mass %

	Probe scale	Thermocouple scale	
	non-mag	non-mag	mag
Ca	21.4	19.6	1.35
S	11.3	-	1.5
Fe	5.0	-	-
V	0.44	0.42	0.05
Ni	0.3	-	-

The concentrations of V and Ca are very similar in both non-magnetic samples. The Ca concentration is in the same range as is found in the ash streams from the combustor. The V concentration, however, is about four times higher than is found in the bed or heat exchanger ash, and one and a half times that of the baghouse ash. As shown in Appendix B, the vanadium concentration in the ash increases with decreasing ash particle size. Thus, if the material which makes up the deposit is very small sized particles, the high V concentration in the scale may be explained.

The magnetic sample, which would represent material spalled off from the metallic surface, has much lower concentrations of Ca, S, and V. The sulphur concentration is higher than can be accounted for as $CaSO_4$, and is probably associated with chromium.

Examination of Corrosion Probes

The sets of three probes from the Syncrude and from the Minto combustion tests were submitted for examination to the Corrosion Science Section of the Physical Metallurgical Research Laboratories (PMRL). Although the examination of these probes has been reported by Gilmour (14), the main findings will be repeated here. The following information is taken from Gilmour's report.

Figures 6 and 7 show the tops and bottoms of both sets of tubes. Set 1, from the Syncrude tests, had significant deposits on the bottoms of all tubes. Some of the deposit had spalled, particularly from the bottom center areas of all tubes. The tops of all three tubes had no adherent deposit, but were covered with a thin scale overlain with a dusty deposit.

The tubes from the Minto coal tests, Set 2, appeared somewhat different from Set 1 in that, although the bottoms were dull red and scaled, there was little obvious deposit retained. The tops were similar to those of Set 1 and were covered with a thin scale and dusty deposit.

Figures 10 and 11 are of polished cross sections from those portions of tubes located at the center of the combustor diameter. There was little corrosive attack on the tops of the tubes, other than a few minor grain boundary scale intrusions about 5 um deep. All tubes exhibited considerable intergranular corrosion, to a depth of about 70 um, on the bottoms where there were, or had been, deposits. The depth of attack was more uniform on Set 1 tubes (Syncrude coke) than on Set 2 tubes (Minto coal). The maximum depth of attack occurred on the middle tube of Set 2 where scale intrusion and precipitates of oxides and sulphides extended up to 120 um into the specimen along grain boundaries. There appeared to be little difference in the type of attack observed in all the samples, and that attack was always associated with surface deposits, or areas where there had been deposits. There was no evidence of erosion.

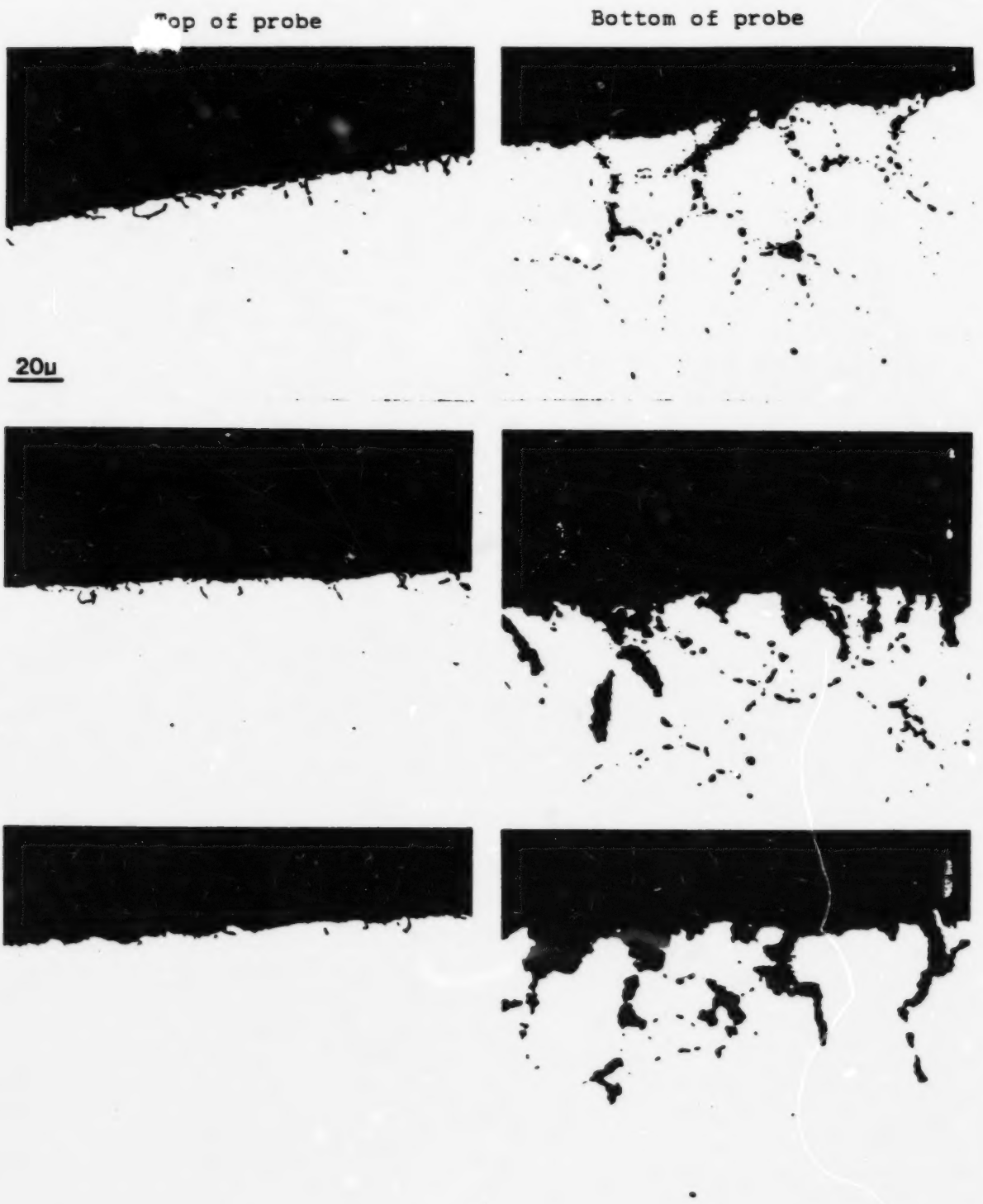


Fig. 10 - Photomicrographs of sections from the tops and bottoms of probes from Syncrude runs

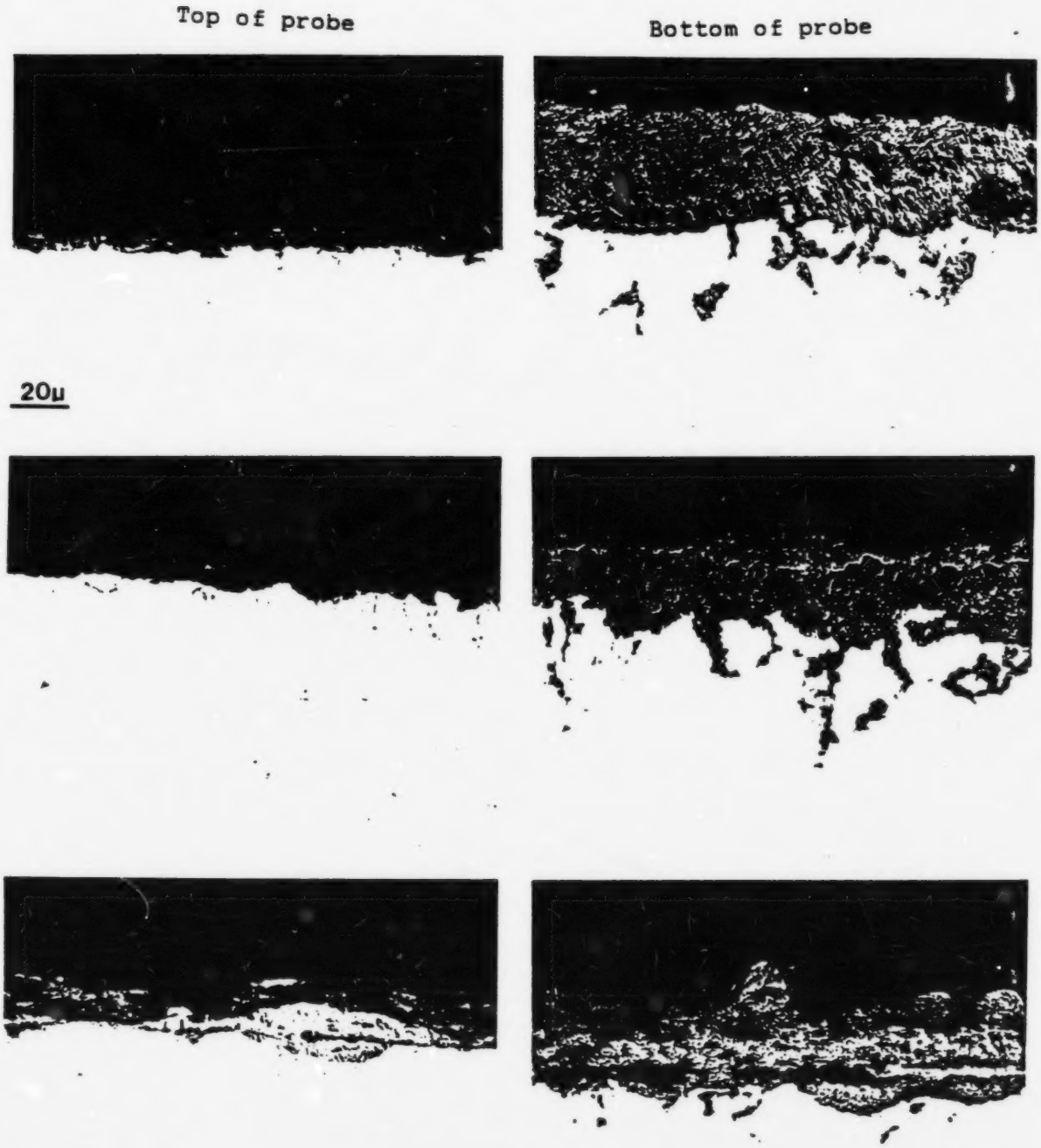


Fig. 11 - Photomicrographs of sections from the tops and bottoms of probes from Minto runs

Electron Probe Microanalysis

Samples of tubes were examined by electron probe microanalysis by the Metals Physics Section of PMRL. The results are given in Figures 12 to 14, which show X-ray maps for the elements of interest. The analyses of both sets of tubes are very similar. The alloy scale and large intrusions are very rich in chromium and are probably Cr_2O_3 containing significant amounts of sulphur and silicon. The sulphur has penetrated into the alloy along the grain boundaries and probably precipated as CrS. The alloy adjacent to these precipitates is depleted of chromium and therefore appears enriched in nickel. The corrosion product scale is covered with a deposit that is rich in calcium, but appears to be rather low in sulphur, Figures 13 and 14. No vanadium was found in the deposit or corrosion products on the tubes exposed in the Syncrude coke trials.

Discussion of Probe Investigation

There are two main findings from this investigation. First, the vanadium in the Syncrude coke does not appear to effect the corrosion of Type 304 SS at combustion temperatures normally employed in a circulating fluidized bed combustor. As no vanadium was found in the corrosion products and only a minor amount in the deposit (as determined by chemical analysis), it is difficult to believe that the vanadium content of the coke influenced the deposit formation or corrosion. Any small quantity of vanadium present (<0.5%) in the deposit most probably exists as calcium vanadate. In reported cases where vanadium contributed to tube corrosion, there was evidence that the

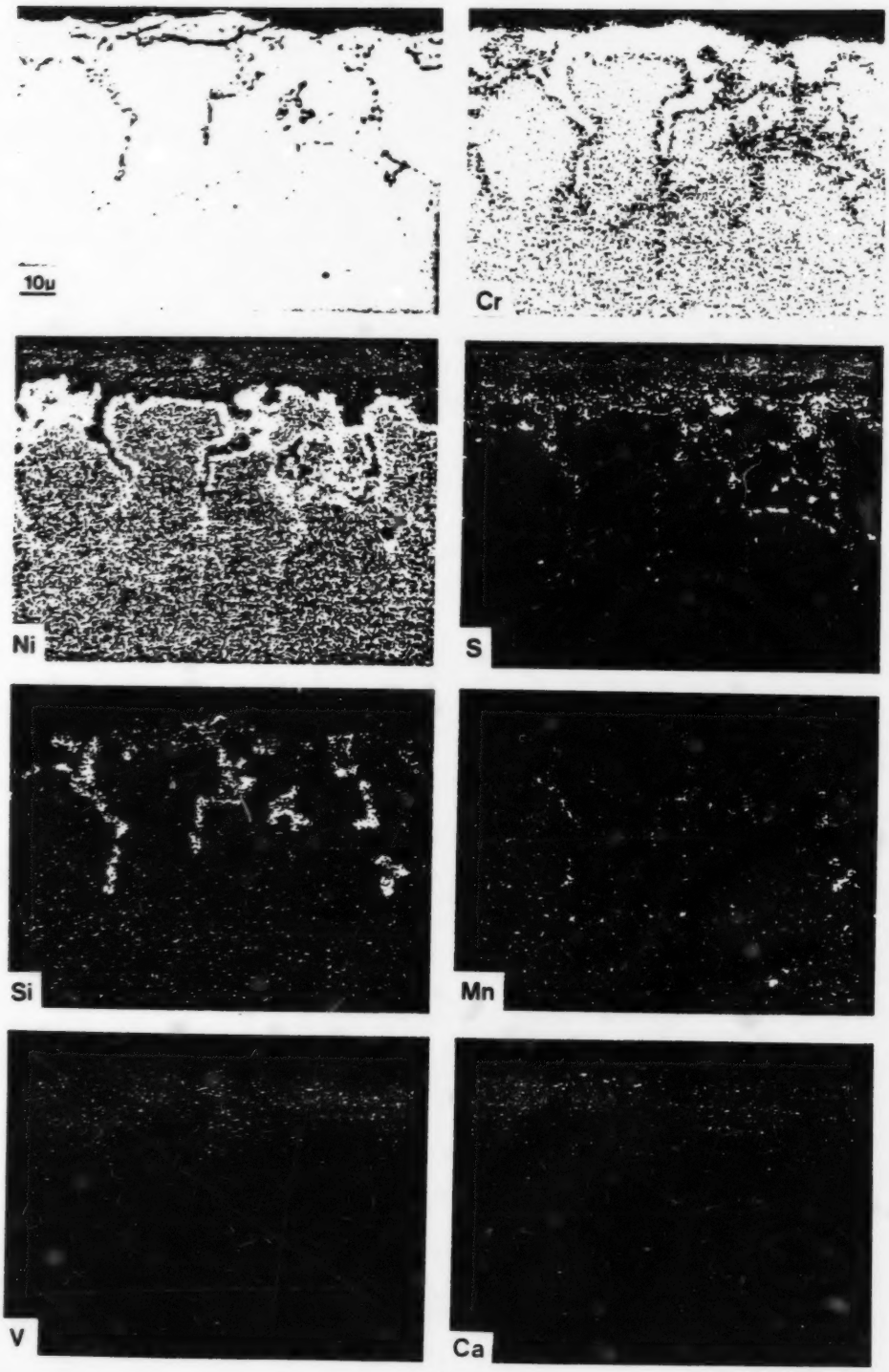


Fig. 12 - Electron image and X-ray maps for a section from the bottom of the bottom tube of Syncrude runs

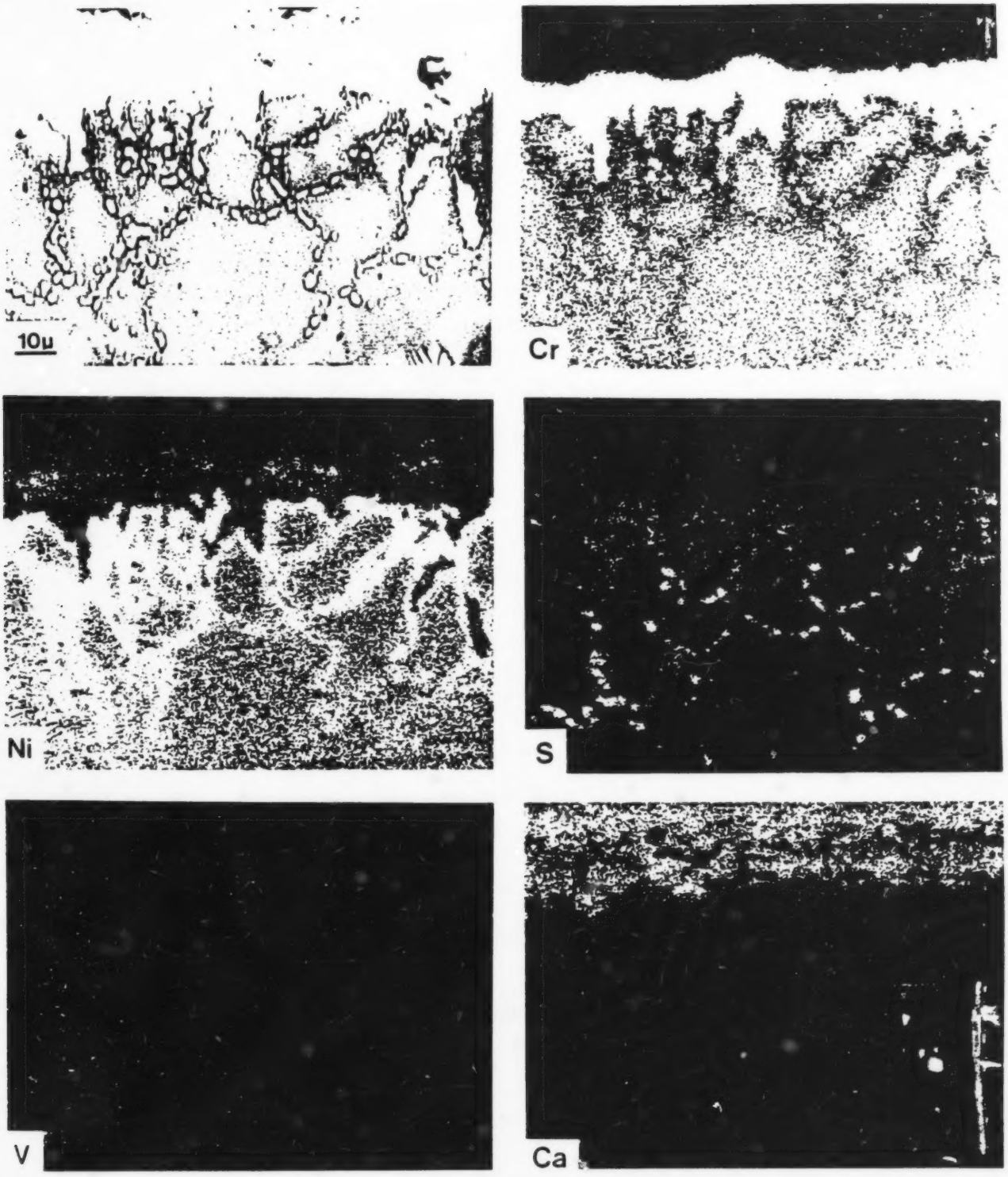


Fig. 13 - Electron image and X-ray maps for a section from the bottom of the middle tube of Syncrude runs

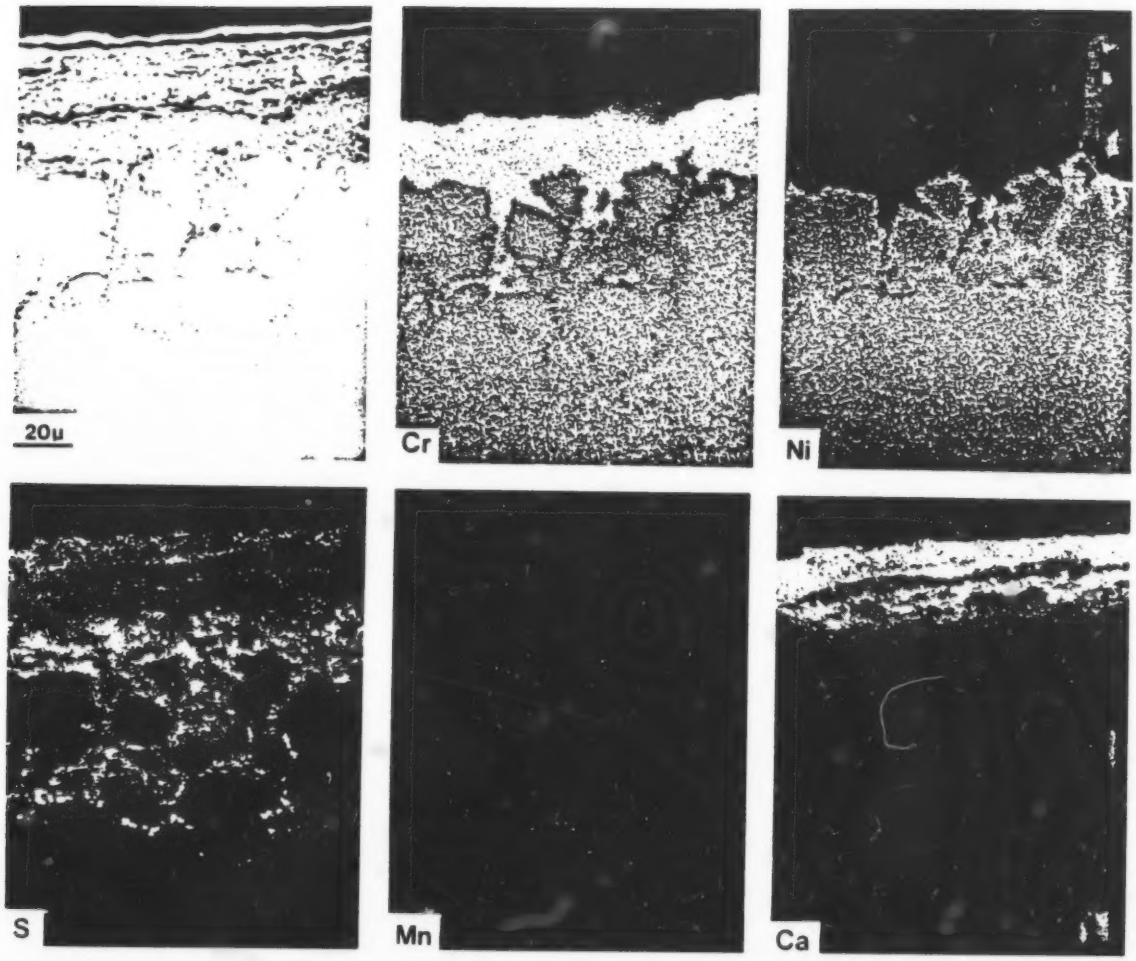


Fig. 14 - Electron image and X-ray maps for a section from the bottom of the middle tube of Minto runs

deposit had been a liquid with a melting point of 500 - 650°C and the V_2O_5 concentration was 20-34% (4).

The second important result is that corrosion beneath deposits in this circulating fluidized bed combustor is very similar to that observed on in-bed tubes in bubbling-bed combustors (15). It appears that the mechanism of attack in the two types of fluidized bed combustors is the same and is probably similar to that described by Stringer and Ehrlich (16). They proposed that if a calcium sulphate-containing deposit forms on an alloy, and if the permeability of the deposit is very low, then the activity of sulphur at the scale-deposit interface is established by the Ca-O-S system. That is, the partial pressure of sulphur is higher than that of oxygen. Calculations have shown that if local equilibrium is established between $CaSO_4$ and the alloy, the predicted phases are usually those found in corrosion products of stainless steels exposed in FBCs.

Although the probes were exposed for only 125 h, the corrosion was fairly severe such that 304 SS would not be suitable material to use in a CFBC at 850°C. CFBCs do not have in-bed heat-transfer tubes in the bed as do AFBCs. Water-wall tubes are usually used for heat transfer in CFBCs, and while it is possible that deposits could form on the tubes, the metal temperature is so much lower than the combustor that corrosion problems are unlikely. In addition, water-walls would be fabricated of a carbon steel, not an austenitic stainless steel, and would not be susceptible to the type of attack reported here.

CONCLUSIONS

Syncrude coke, with Fort McMurray limestone sorbent, and Minto coal, with New Brunswick limestone sorbents, were combusted in a 100 mm diameter, 2800 mm high pilot-scale circulating fluidized bed combustor. The principal purpose of this project was to investigate the emissions of SO_2 and heavy metals, their capture with limestone sorbents and metallic corrosion. In the Syncrude coke trials, with a Ca/S molar ratio = 2.0, greater than 90% of the sulphur was captured and 93% of the vanadium and 106% of the nickel were accounted for in the ashes. Combustion efficiency was 96%. Combustion trials with Minto coal and New Brunswick limestones resulted in lower than expected sulphur capture and combustion efficiency. The combustion efficiency was 88%. Both sources of limestone, Elmtree and Havelock, captured 70-75% of the SO_2 with a Ca/S mole ratio = 2.0. Depending on the New Brunswick limestone source and particle size distribution, up to 40% passed through the combustor without calcining. The recommended limestone for use at the Chatham CFBC is either quarry of Elmtree Resources.

A set of three type 304 stainless steel tubes were exposed for 125 hours at the combustor operating temperature of 850°C for each fuel. Deposits were found on the bottom area of all tubes. Metallographic examination showed that all tubes suffered intergranular sulphidation/oxidation corrosion in the areas where the deposits had formed. The degree and type of corrosive attack was the same for the Syncrude and Minto trials, and was also identical to that found in atmospheric bubbling bed FBC units.

There was no evidence of accelerated corrosion attributable to the vanadium content of the coke.

The heavy metals concentrate in the fine ash collected in the baghouse. Attempts to extract vanadium by a salt-roast/leach were unsucessful. An analysis of the thermodynamics by the FACT system indicated that the vanadium should react with the limestone to form calcium vanadate which is a stable, high melting point compound.

ACKNOWLEDGEMENTS

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APPENDIX A

Material Balance - Syncrude Coke Runs

	IN (kg)		OUT (kg)			
Run	Feed	Theo ash	Ash	- Correction		% Recovery
010486	IB 7000	7110	FB 7945	O2	564	
	C-L 20454	6075	HX 3460		587	
	Coal 4000	444	BH 3865		465	
		13629	15270		1616	100.2
020486	IB 7000	7000	FB 8525	O2	747	
	C-L 21020	6243	HX 3887		373	
	Coal 4000	444	BH 3115		660	
		13687	15527		1780	100.4
030486	IB 7000	7000	FB 8910	O2	1130	
	C-L 26023	7729	HX 6050		1026	
	Coal 3755	417	BH 4005		481	
		15146	18965		2637	107.8
040486	IB 7000	7000	FB 8425	O2	849	
	C-L 21125	6472	HX 4428		750	
	Coal 5243	582	BH 3685		442	
		14856	16538		2041	97.6
080486	IB 7000	7000	FB 8700	O2	1115	
	C-L 36364	10800	HX 6970		1182	
	Coal 6544	726	BH 5840		701	
		18526	21510		2998	99.9
090486	IB 7000	7000	FB 8836	O2	903	
	C-L 22898	6800	HX 5085		862	
	Coal 4337	481	BH 3655		439	
		14281	17576		2204	107.6
100486	IB 7000	7000	FB 8960	O2	964	
	C-L 25454	7560	HX 4835		720	
	Coal 5067	562	BH 4785		574	
		15122	18580		2358	107.3
220486	IB 7000	7000	FB 10020	O2	747	
	C-L 23068	6851	HX 3660		621	
	Coal 5636	626	BH 3475		417	
		14477	17155		1785	106.2
230486	IB 7000	7000	FB 9870	O2	813	
	C-L 23864	7088	HX 2655		450	
	Coal 4800	532	BH 3560		427	
		14620	16085		1690	98.5

Material Balance (con't) - Syncrude Coke Runs

	IN (kg)		OUT (kg)			
Run	Feed	Theo ash		Ash -	Correction	% Recovery
240486	IB 7000	7000	FB	10320	O2 983	
	C-L 27273	8100	HX	4220	715	
	Coal 4360	484	BH	4230	508	
		15584		18770	2206	106.3
250486	IB 7000	7000	FB	9250	O2 922	
	C-L 26932	7999	HX	4640	787	
	Coal 4425	491	BH	4365	524	
		15490		18255	2233	103.4
120586	IB 7000	7000	FB	5250	O2 464	
	C-L 27386	8134	HX	5370	910	
	Coal 5500	610	BH	4320	518	
		15744		14940	1894	82.9
140586	IB 7000	7000	FB	6935	O2 811	
	C-L 25341	7526	HX	6035	1023	
	Coal 5330	592	BH	4255	511	
		15118		17225	2345	98.4
150586	IB 7000	7000	FB	8585	O2 887	
	C-L 26022	7729	HX	4880	827	
	Coal 6274	696	BH	4955	595	
		15425		18420	2309	104.4
160586	IB 7000	7000	FB	8605	O2 1234	
	C-L 29378	8725	HX	6610	1121	
	Coal 4675	519	BH	4950	594	
		16244		20165	2949	106.0
			overall average (excluding 120586)			103.3

Note: IB = initial bed, C-L = cokeand limestone blend, Coal = startup coal, FB = final bed, HX = heat exchanger, BH = baghouse, O2 = correction due to oxidation of SO3

Run 120586 was excluded due to the accidental loss of some bed material

APPENDIX B

Chemical Analysis of Syncrude Coke Ash

Table B1 - Chemical analysis of bed material

Run	Sample	Ca	S	V	Ni	C
010486	0955-1430	19.62	9.59	.08	.04	0.2
020486	1035-1500	21.21	10.84	.08	.06	0.2
030486	1000-1500	23.74	12.81	.11	.04	0.4
040486	1000-1430	24.61	13.71	.09	.04	0.9
080486	1020-1445	26.96	13.41	.08	.05	1.1
090486	1000-1500	24.79	13.84	.09	.06	0.9
110486	1000-1500	24.57	13.70	.09	.05	
220486	1000-1500	26.58	13.38	.13	.05	
230486	1000-1500	28.41	13.85	.10	.04	
240486	0925-1500	26.77	13.68	.12	.04	
250486	0905-1500	27.12	13.72	.11	.04	
120586	0915-1440	25.82	14.29	.08	.02	
140586	0920-1420	27.41	14.15	.07	.03	
150586	1000-1500	25.70	13.58	.09	.03	
160586	0910-1440	26.08	14.56	.08	.03	
Average		25.29	13.27	.09	.04	

Table B2. - Chemical analysis of heat exchanger drain

Run	Sample	Ca	S	V	Ni	C
010486	0955-1430	24.09	8.05	.12	.06	14.9
020486	1035-1125	20.18	8.17	.11	.06	
	1125-1500	20.23	8.87	.12	.07	
030486	1000-1500	22.96	8.75	.13	.07	
040486	1000-1430	22.87	9.01	.11	.06	
080486	1020-1445	21.93	8.74	.12	.07	
090486	1000-1500	20.88	8.49	.12	.06	
110486	1000-1500	19.97	9.05	.12	.06	
220486	1000-1500	19.99	7.75	.14	.07	
230486	1000-1500	22.16	7.64	.14	.07	
240486	0925-1200	20.40	7.29	.14	.07	
	1200-1500	22.08	8.14	.15	.07	
250486	0905-1200	20.02	7.69	.14	.06	
	1200-1500	20.96	9.41	.15	.06	
120586	0915-1440	20.14	9.06	.12	.06	
140586	0920-1200	23.73	8.50	.11	.05	
	1200-1420	22.09	10.26	.12	.05	
150586	1000-1200	17.82	8.77	.10	.04	
	1200-1500	20.11	9.24	.13	.06	
160586	0910-1200	18.20	8.31	.10	.05	
	1200-1440	21.11	10.50	.12	.05	12
Average		21.06	8.65	.12	.06	

Table B3. - Chemical analysis of baghouse

Run	Sample	Ca	S	V	Ni	C
010486	0955-1430	21.03	4.59	.24	.13	
020486	1035-1125	18.98	4.28	.15	.08	
	1125-1500	23.63	5.23	.26	.14	
030486	1000-1500	21.71	5.47	.30	.16	
040486	1000-1430	19.61	5.22	.25	.14	6
080486	1020-1445	21.64	5.12	.28	.14	
090486	1000-1500	19.69	5.23	.26	.14	
110486	1000-1500	18.95	5.63	.26	.14	
220486	1000-1500	21.57	4.97	.27	.14	
230486	1000-1500	20.80	5.05	.28	.15	
240486	0925-1200	22.54	4.74	.24	.12	
	1200-1500	23.62	5.14	.31	.16	
250486	0905-1200	18.09	4.50	.23	.12	
	1200-1500	21.21	5.31	.36	.18	
120586	0915-1440	20.24	5.00	.29	.14	
140586	0920-1200	19.29	4.74	.26	.12	
	1200-1420	30.32	5.81	.37	.17	
150586	1000-1200	19.33	5.18	.23	.11	
	1200-1500	21.03	5.74	.36	.17	
160586	0910-1200	16.67	4.98	.25	.12	
	1200-1440	20.38	6.02	.36	.18	3
Average		20.97	5.14	.28	.14	

APPENDIX C

Chemical Analysis of Minto Coal Ash

Table C1. Chemical analysis of bed material

Run	Limestone	Ca	S
860919	Sormony 1.6	36.78	10.51
860925	" "	36.94	10.14
860929	Stastrong "	37.11	11.04
860930	" "	36.51	10.91
861001	P Rocher "	38.06	11.51
861002	" "	38.53	12.39
861008	Sormony F "	38.50	12.47
861016	" "	36.75	11.68
861017	L Dust "	35.40	11.67
861020	"	34.90	11.48
861028	Sormony "	36.82	11.1
861030	" 2.0	38.71	11.3
861103	Stastrong "	38.30	10.5
861106	" 1.6	37.08	12.7
861107	" C "	37.30	12.79
861110	Sormony "	18.59	4.81
861112	P Rocher "	26.31	7.21
861113	" 2.0	33.23	8.74
861114	Stastrong C "	36.86	12.06

Table C2. Chemical analysis of heat exchanger drain

Run	Limestone	Ca	S	C	CO2
860919	Sormony 1.6	12.97	3.87		
860925	" "	15.71	3.67		
860929-1	Stastrong "	24.30	3.24		
-2		28.06	4.26	14.14	13.17
860930-1	" "	26.80	3.72		
-2		27.30	4.17	16.46	11.33
861001-1	P Rocher "	25.87	4.46		
-2		23.99	5.02	13.65	5.92
861002-1	" "	21.47	5.06		
-2		23.02	4.96	13.85	4.90
861008-1	Sormony F "	21.74	4.30		
-2		24.75	5.12	11.15	6.66
861016-1	"	21.91	3.75		
-2		23.60	4.93	13.10	8.48
861017-1	L Dust "	27.66	4.48		
-2		33.35	6.33	9.75	10.02
861020-1	"	29.76	4.78		
-2		31.32	6.58	10.96	10.23
861028-1	Sormony "	18.50	4.97		
-2		16.81	4.37	19.35	4.83
861030-1	" 2.0	20.92	4.69		
-2		20.39	4.58	12.55	3.97

Table C2 (con't). Chemical analysis of heat exchanger drain

Run	Limestone	Ca	S	C	CO2
861103-1	Stastrong 2.0	31.37	4.75		
-2		34.44	6.31	7.90	9.05
861106-1	" 1.6	28.79	4.79		
-2		30.72	5.61	11.82	9.74
861107-1	" C "	30.63	5.47		
-2		30.30	6.07	11.45	6.88
861110-1	Sormony "	20.34	4.57		
-2		17.22	4.24	23.35	4.62
861112-1	P Rocher "	15.87	3.16		
-2		17.93	4.18	17.95	4.27
861113-1	" 2.0	18.61	3.73		
-2		20.35	4.11	18.15	5.72
861114-1	Stastrong C "	24.00	4.42		
-2		28.12	5.58	12.40	7.24

Table C3. Chemical analysis of baghouse ash

Run	Limestone	Ca	S	C	CO2
860919-1	Sormony 1.6	8.74	3.03		
-2		9.60	2.73	32.65	3.39
860925	" "	10.18	2.92		
860929-1	Stastrong "	13.72	2.56		
-2		15.18	3.04	26.10	7.72
860930-1	" "	15.77	3.02		
-2		16.67	3.22	23.85	7.36
861001-1	P Rocher "	12.84	3.20		
-2		13.09	3.33	25.37	4.84
861002-1	" "	11.37	3.46		
-2		11.69	3.14	26.95	3.98
861008-1	Sormony F "	17.64	3.32		
-2		14.45	3.56	23.65	7.28
861016-1	Sormony F "	13.73	3.05		
-2		14.71	3.25	24.90	8.71
861017-1	L Dust "	17.64	3.32		
-2		21.47	3.77	20.65	10.92
861020-1	"	19.53	3.50		
-2		21.92	4.24	20.85	12.23
861028-1	Sormony "	11.14	3.67		
-2		11.38	3.40	30.28	4.85
861030-1	" 2.0	13.29	3.96		
-2		13.12	3.68	24.90	4.89
861103-1	Stastrong 2.0	18.74	3.74		
-2		22.19	4.30	19.60	9.61
861106-1	" 1.6	18.52	4.24		
-2		19.82	4.02	22.45	8.84
861107-1	" C "	17.87	4.20		
-2		18.04	4.22	23.15	5.42
861110-1	Sormony "	14.21	4.26		
-2		12.56	3.54	30.00	4.66
861112-1	P Rocher "	11.10	3.62		

Table C3 (con't). Chemical analysis of baghouse ash

Run	Limestone	Ca	S	C	CO2
861112-2		10.79	3.37	31.15	3.71
861113-1	" 2.0	11.10	3.69		
-2		12.44	3.56	28.75	4.16
861114-1	Stastrong C "	12.73	4.26		
-2		13.97	3.83	25.95	4.77